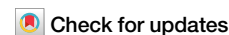




EuCl₃-mediated corrosion of Ni and Ni-20Cr model alloy in LiCl-KCl molten salt



Kaustubh Bawane¹✉, Yuxiang Peng², Linu Malakkal³, Mario Matos¹, William Phillips⁴, Katsuyo Thornton⁵, James F. Wishart⁶, Yu-chen Karen Chen-Wiegart^{2,7} & Ruchi Gakhar⁴✉

Corrosion of structural materials is a key engineering challenge for the development of molten salt reactors (MSRs). Metal ion impurities in the salt, which are inevitable due to their natural evolution in a reactor (e.g., fission products, corrosion products, etc.) can significantly impact the corrosion performance of structural materials. In this work, we investigated the effects of one fission product, Eu in its 3+ oxidation state, on the corrosion behaviors of pure Ni metal and Ni-20Cr model alloy in molten LiCl-KCl eutectic using in situ optical spectroscopy, post-corrosion inductively coupled plasma mass spectrometry (ICP-MS), and electron microscopy-based techniques. The EuCl₃-containing salt was found to be extremely corrosive to both Ni and Ni-20Cr. Detailed microstructural characterization revealed that pure Ni primarily exhibited planar corrosion fronts with occasional shallow intergranular attacks, while Ni-20Cr alloy showed severe localized intergranular attacks with selective Cr leaching and salt penetration near grain boundaries. Additionally, this study uncovered the unique intragranular crystallographic attack of Ni-20Cr under exposure to EuCl₃-containing salt. Overall, these findings are crucial for understanding how oxidizing salt impurities such as EuCl₃ affect corrosion reactions and diffusion kinetics at the salt-material interface, thereby influencing corrosion microstructure evolution pathways.

Molten metal halide salts are prime candidates for use as high-temperature heat transfer fluids in concentrated solar power (CSP) plants¹, molten salt reactors (MSRs)^{2,3}, and electrochemical media for pyrochemical processing of spent nuclear fuel, metal extraction, batteries and catalysis^{4–7}. MSR technology stands out amongst Generation IV nuclear reactor concepts as it uses a mixture of molten salt coolant and soluble fuel that circulates between the reactor core and the heat exchanger. While many MSR designs utilize fluoride salts, chloride salts have gained attention for fast reactors due to the low neutron moderation of chlorine. Molten chloride salts offer advantages such as lower melting temperatures, higher solubility of fissile materials, and lower costs compared to fluoride-based systems^{8,9}. However, corrosion of structural materials in the presence of molten chlorides remains a significant challenge. Understanding material degradation under extreme environments offered by molten salt is therefore critical for the development and demonstration of sustainable energy systems such as MSRs^{10–12}.

The native passive oxide layers formed on many structural alloys help them resist corrosion in high-temperature, oxygen-containing

environments. However, these passive oxide layers are reported either to not form or to lose their protective ability in molten halide salts, according to the literature^{12–14}, leading to corrosion degradation through direct interfacial reactions between bare alloy and salt. Corrosion in molten salts is influenced by a variety of factors including thermodynamics, the presence of oxidizing salt impurities, gradients in activity, solubility, temperatures and residual stresses, irradiation damage, and galvanic effects due to secondary phases in the structural alloy^{10–12,14–19}. Redox potential vs. temperature diagrams indicate that alkali chlorides are very stable and thermodynamically should not have any reaction with structural materials¹¹. Nevertheless, even well-purified salt in MSRs will contain impurities such as fission products from fuel burnup, including rare earth elements such as La, Nd, Ce, Eu, Pr, Sm, etc.²⁰, which can enter molten salts as stable ions, corrosion products (e.g. metal ions like Ni²⁺, Cr²⁺, Cr³⁺, and Fe³⁺, etc.)^{21–23}, and moisture, given the hygroscopic nature of some chloride salts¹⁰. Many of these impurities are known to severely accelerate the corrosion of structural alloys by increasing the oxidation potential of molten salt^{24–28}. Among these rare earth fission

¹Nuclear Materials Performance Division, Idaho National Laboratory, Idaho Falls, ID, USA. ²Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY, USA. ³Computational Mechanics and Materials Department, Idaho National Laboratory, Idaho Falls, ID, USA. ⁴Advanced Technology of Molten Salts Department, Idaho National Laboratory, Idaho Falls, ID, USA. ⁵Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI, USA. ⁶Chemistry Division, Brookhaven National Laboratory, Upton, NY, USA. ⁷National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY, USA. ✉e-mail: kaustubh.bawane@inl.gov; ruchi.gakhar@inl.gov

products, Eu is unique in possessing two salt-stable oxidation states (Eu^{2+} and Eu^{3+}) in molten chloride salts, whereas most others (La, Nd, Ce, Pr, Sm) are stable only as $3+$ ions and therefore lack a readily accessible reduction pathway to drive oxidation of structural metals.

Previous reports have demonstrated various microstructures observed during molten salt corrosion of structural alloys. Common microstructural features reported in the literature include grain boundary (GB) attack (intergranular corrosion), selective leaching of the most electrochemically susceptible alloying elements (e.g., chromium (Cr)), resulting in their depletion followed by void formation and salt penetration along GBs, and percolation dealloying. In our previous work, we directly visualized intergranular corrosion and Cr depletion in Ni-20Cr alloy during both early and later stages of molten salt corrosion in KCl-MgCl₂ salt using novel quasi in situ transmission electron microscopy (TEM) and in situ synchrotron 3D nanotomography techniques²⁹. Recently, Yang et al.³⁰ proposed a new mechanism called ‘wormhole’ type intergranular corrosion, where parts of GBs in Ni-20Cr alloy were attacked in an interconnected wormhole fashion after exposure to molten fluoride salt. Liu et al.³¹ observed percolation dealloying-type bi-continuous salt-filled porous structures during in situ synchrotron 3D tomography studies of Ni-20Cr exposed to KCl-MgCl₂ salt at 800 °C. In contrast, at lower temperatures (500–600 °C), the same system exhibits intergranular corrosion, likely due to the relative rates of diffusion of elements/ion species and reaction rates at the salt-metal interface for the different microstructure evolution pathways observed during molten salt corrosion¹⁶.

Metal ion additives in molten salts can directly influence corrosion behavior, including morphological evolution, due to their redox potentials relative to structural metals and their ability to modify interfacial chemical kinetics and mass transport rates²¹. For example, the fission product europium (Eu) has two salt-stable oxidation states, Eu^{2+} and Eu^{3+} . In molten chloride salts, the formal potential of the $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox couple is considerably more positive than the redox couples of Ni, Fe, and Cr, the primary components of structural alloys^{32–34}. A more positive $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox couple suggests that Eu^{3+} has a strong tendency to reduce to the Eu^{2+} state. Consequently, Eu^{3+} acts as a potent oxidant, facilitating the oxidation of these metals and leading to their accelerated dissolution in the salt. Guo et al.³² studied the corrosion of Alloy 709 stainless steel and Inconel 718 Ni-based superalloy in LiCl-KCl eutectic molten salt with added EuCl_3 . The addition of EuCl_3 caused severe dissolution of alloying elements as well as intergranular and intragranular cracking in both alloys. Chang et al.²⁵ reported that the addition of 2% EuCl_3 increased the corrosion rate of commercial alloys like Haynes C276, Inconel 600, Inconel 800, and SS316L by over two orders of magnitude. These early reports clearly established the detrimental effects of Eu^{3+} on the corrosivity of molten chloride salts. However, they did not report a detailed analysis of the mechanisms behind the interfacial and microstructural evolution of the structural alloy. Further systematic studies are needed to identify how the reactivity of Eu^{3+} impacts salt and alloy chemistries, reactions at the interface and thereby microstructural evolution during molten salt corrosion.

In this study, we utilized in situ optical spectroscopy along with post-corrosion ICP-MS to investigate the evolution of salt chemistry during the corrosion of Ni and Ni-20Cr model alloy in molten LiCl-KCl salt, both in the absence and presence of 1 wt% EuCl_3 . To gain a deeper understanding of the corrosion mechanisms, we examined the nanoscale microstructural and chemical evolution at the interface of corroded Ni and Ni-20Cr samples using scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDS), precession electron diffraction (PED) and electron energy loss spectroscopy (EELS) techniques. Additionally, we employed the three-dimensional (3D) focused ion beam-equipped scanning electron microscopy and EDS (3D FIB-SEM-EDS) tomography technique to visualize and analyze the complex localized corrosion features, particularly in Ni-20Cr exposed to EuCl_3 -containing salt. Our goal is to fundamentally understand the physicochemical processes at the salt-material interface that govern microstructural evolution in Ni-based model systems (Ni and Ni-20Cr alloy) under exposure to molten chloride

salts with oxidizing additives like EuCl_3 . This fundamental study provides insights that will inform corrosion modeling and simulation, as well as guide future strategies to understand and mitigate the corrosion of complex engineering alloys in molten salts in the presence of impurities.

Results and discussions

In situ optical spectroscopy measurements during corrosion

The optical spectra of the molten LiCl-KCl and LiCl-KCl-1wt% EuCl_3 salts after the addition of Ni and Ni-20Cr wires are shown in Fig. 1. Figure 1a and b display the spectral monitoring of Ni wire dissolution in LiCl-KCl and LiCl-KCl-1wt% EuCl_3 molten salts, respectively. It is evident that absorption peaks corresponding to Ni^{2+} (due to Ni dissolution) are detectable only in the LiCl-KCl-1wt% EuCl_3 mixture. Similarly, for Ni-20Cr, a clear growth of Ni^{2+} absorption spectra is evident in the LiCl-KCl-1wt% EuCl_3 mixture (Fig. 1d). The absence of any detectable Ni^{2+} in systems without EuCl_3 (Fig. 1a and c) demonstrates that EuCl_3 plays a crucial role in promoting the oxidative dissolution of both Ni and Ni-20Cr. Comparing the dissolution of Ni and Ni-20Cr wires in LiCl-KCl-1 wt% EuCl_3 (Fig. 1b and d), it is evident that the Ni^{2+} absorption peaks for Ni metal are much stronger as compared to the Ni-20Cr alloy. It is worth noting that Cr^{2+} and Cr^{3+} ions were not detected in the optical spectra during the dissolution of Ni-20Cr wire in both LiCl-KCl and LiCl-KCl-1 wt% EuCl_3 (Fig. 1c and d). The lack of observed Cr^{2+} and Cr^{3+} peaks in the salt could be explained by the formation of Cr oxide particles, as shown later in Section 3.3 (see Fig. 6).

Chemical analysis of salt after corrosion using ICP-MS

To determine the concentration of Ni and Cr species corroded into the salt, the post-corrosion solidified salt was analyzed with the ICP-MS technique. After the corrosion of Ni wire, the LiCl-KCl salt showed negligible dissolution of Ni at 0.048 ppm, compared to a significantly higher 39.8 ppm in the LiCl-KCl-1wt% EuCl_3 salt. This indicates that the addition of 1 wt% EuCl_3 in LiCl-KCl increased the dissolution of Ni by approximately ~800 fold for the Ni wire sample. Similarly, for Ni-20Cr wire, dissolution of Ni into LiCl-KCl salt was 0.036 ppm, while it was substantially higher (over ~600 fold) at 22.8 ppm in LiCl-KCl-1wt% EuCl_3 . The dissolution of Cr from Ni-20Cr wires into LiCl-KCl and LiCl-KCl-1wt% EuCl_3 was 12.8 ppm and 497 ppm, respectively, indicating that the addition of 1 wt% EuCl_3 caused an approximately 40-fold increase in Cr dissolution. It is worth noting that Cr dissolution in both LiCl-KCl and LiCl-KCl-1wt% EuCl_3 was significantly higher than Ni dissolution by ~360 and ~22 fold, respectively. This observation aligns with the widely reported selective leaching of Cr in alloys due to its electrochemically less noble nature.

Post-corrosion characterization using electron microscopy

To gain mechanistic insights into the microstructural and interfacial changes resulting from corrosion, detailed post-corrosion characterization of the Ni and Ni-20Cr samples was carried out using advanced electron microscopy techniques. Figure 2a displays a STEM bright-field image and the corresponding EDS mapping of the interface between pure Ni metal and LiCl-KCl salt after corrosion. The microstructure reveals intergranular corrosion and salt penetration, as indicated by the cyan color arrows in Fig. 2a. The EDS elemental composition results for region 1 (salt region near the interface) and region 2 (Ni metal region near the interface), are shown in the form of doughnut charts in Fig. 2b. The salt region shows significant dissolution of Ni (~20.8 at%) near the interface, along with the notable concentrations of lithium (35.2 at%), chlorine (~10 at%) and oxygen (~33.6 at%), but negligible potassium (~0.3 at%). The significant oxygen content in the salt region could be due to the hygroscopic nature of the salt even in a well-controlled glovebox environment, and it indicates strong involvement of oxygen in corrosion reactions near the interface. As expected, the EDS composition analysis of region 2 (Ni metal) shows elemental Ni at ~96.2 at%.

To assess the impact of EuCl_3 addition, similar characterization was performed on Ni samples corroded in LiCl-KCl-1wt% EuCl_3 . Figure 3a shows a STEM bright-field image and the corresponding EDS mapping of

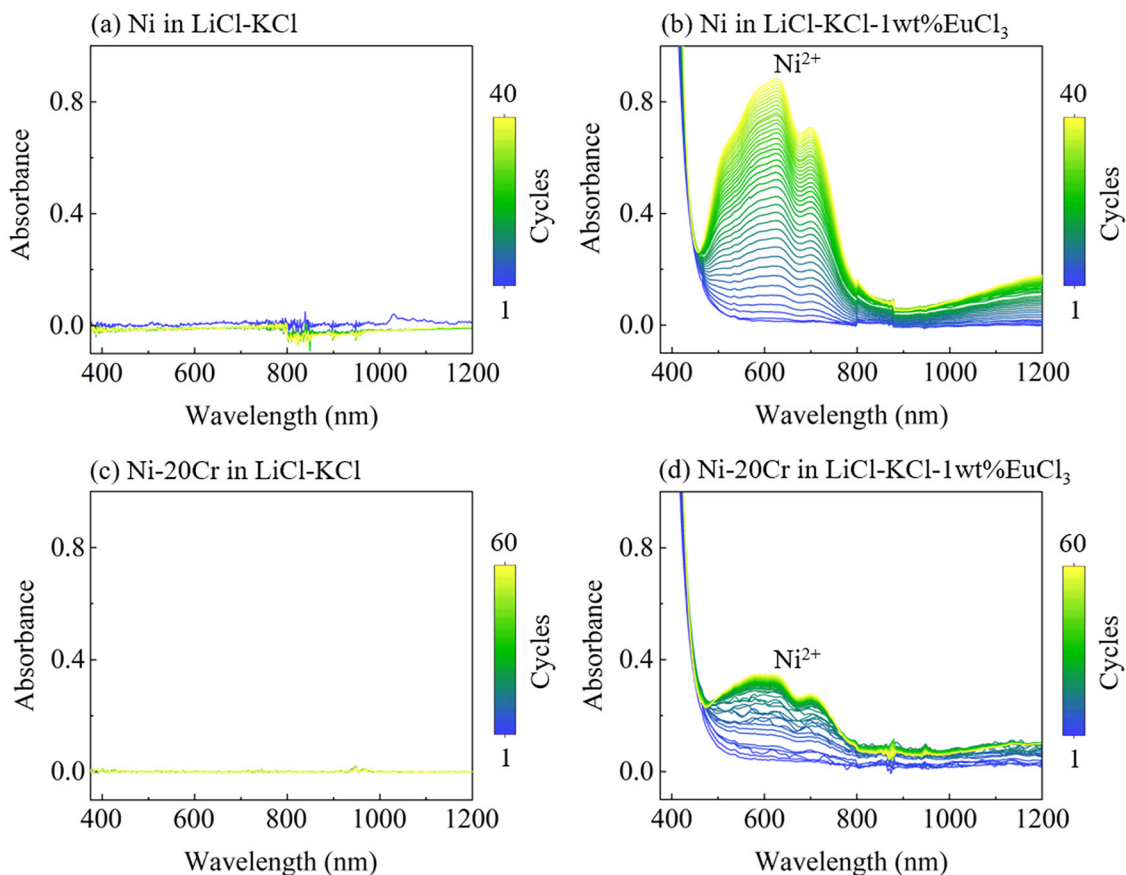


Fig. 1 | In-situ optical spectroscopy during molten salt corrosion. Optical spectra recorded during the in situ corrosion experiments of (a) Ni in LiCl-KCl, (b) Ni in LiCl-KCl-1wt%EuCl₃, (c) Ni-20Cr in LiCl-KCl, and (d) Ni-20Cr in LiCl-KCl-1wt%EuCl₃, at 4-min intervals during isothermal heating at 500 °C.

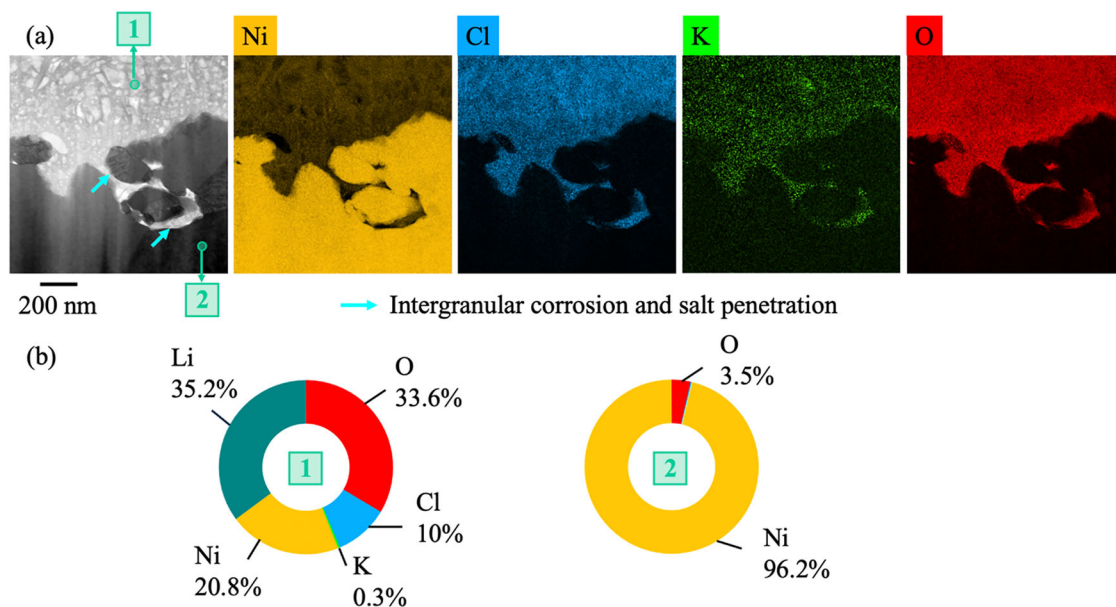


Fig. 2 | STEM-EDS analysis of Ni corroded in LiCl-KCl without EuCl₃. a STEM-bright-field image and corresponding EDS maps of the salt-metal interface, (b) EDS elemental composition (at%) analysis of regions 1 (salt) and 2 (Ni metal).

the interface between LiCl-KCl-1wt%EuCl₃ salt and pure Ni metal. The shallow intergranular attack with salt penetration is evident in the microstructure as indicated by the cyan colored arrows in Fig. 3a. Based on the EDS mapping, salt region is divided into two regions, namely, K-rich (region

1) and Ni- and O-rich (region 2), as shown in Fig. 3a. The Ni metal is represented by region 3. Figure 3b shows the EDS elemental composition analysis of regions 1, 2 and 3. Region 1 constitutes 49.8 at% K and 47.7 at% Cl, closely matching pure KCl, along with small amounts of Ni, Li and O.

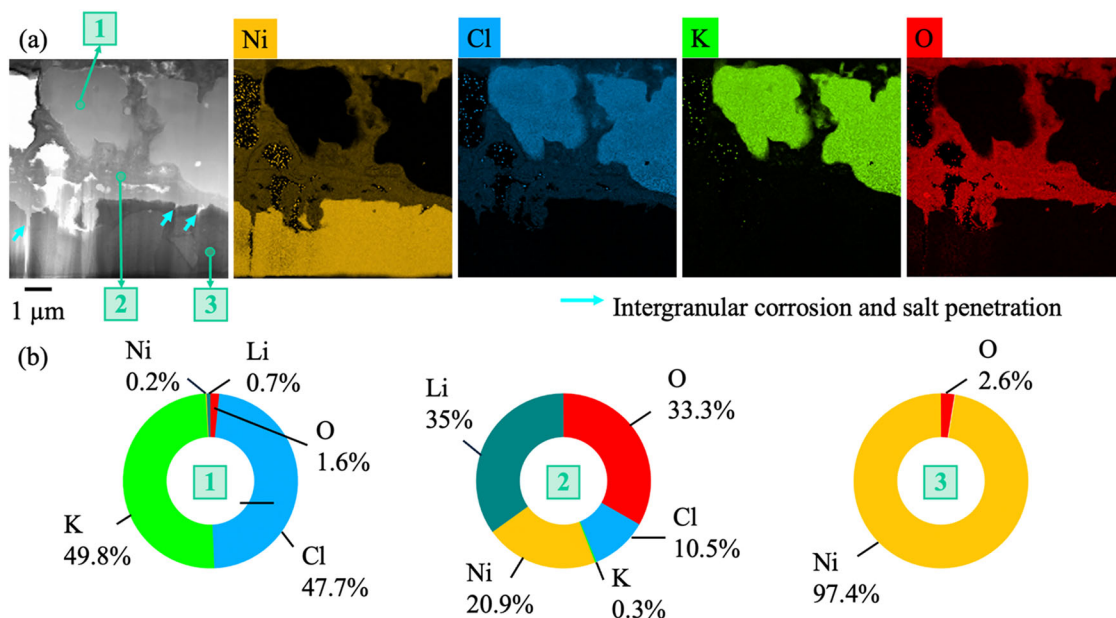


Fig. 3 | STEM-EDS analysis of Ni corroded in LiCl-KCl with 1 wt% EuCl_3 . a STEM bright-field image and corresponding EDS maps of the salt-metal interface, (b) EDS elemental composition analysis of regions 1 and 2 (salt), and 3 (Ni metal).

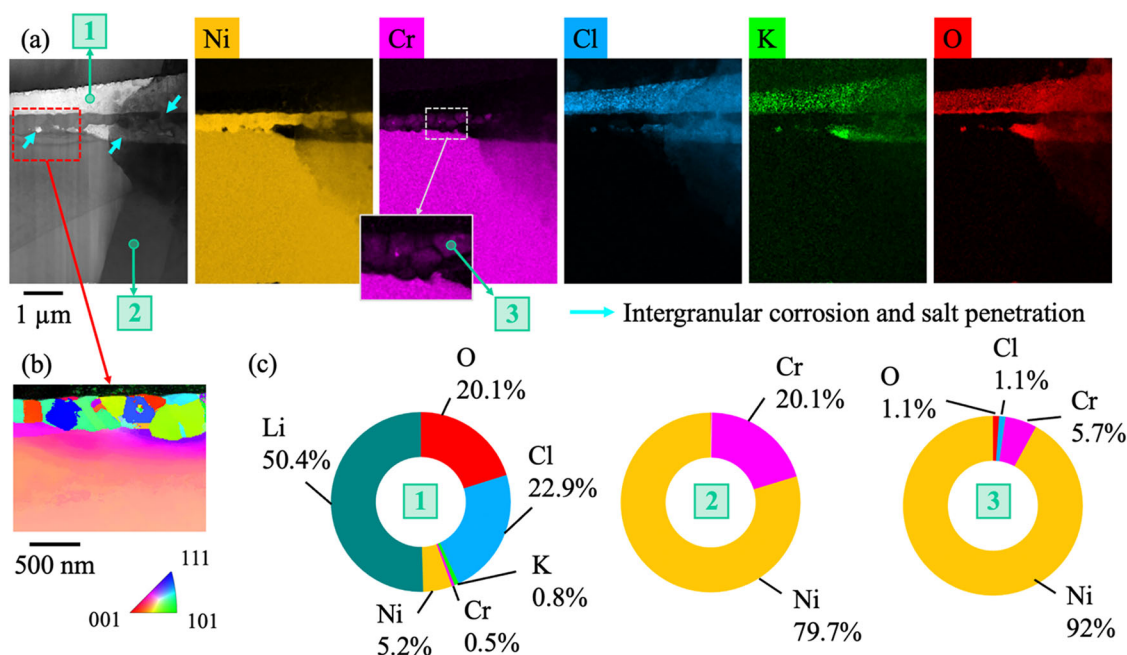


Fig. 4 | STEM-EDS-PED analysis of Ni-20Cr corroded in LiCl-KCl. a STEM bright-field image and corresponding EDS maps of salt-alloy interface at low magnification, (b) PED orientation map of Ni-20Cr from dotted red rectangle region

in Fig. 4a, (c) EDS elemental composition analysis of region 1 (salt), 2 (Cr depleted Ni-20Cr alloy) and 3 (Ni-20Cr alloy).

This provides strong evidence of phase separation of the salt into Li- and K-rich regions during solidification. Consequently, region 2 is Li-rich in addition to Ni and O. EDS results for region 2 show 35 at% Li, 20.9 at% of Ni, 33.3 at% of O and 10.5 at% of Cl and negligible K. This result is similar to what was observed for pure Ni corrosion in blank LiCl-KCl shown in Fig. 2a, b, where Ni and O tend to partition to the Li-rich part of the salt during solidification. It is assumed that this result may not significantly impact corrosion mechanisms because the molten salt itself a well-mixed LiCl-KCl eutectic mixture (blank or with EuCl_3), and elemental partitioning likely occurred only during solidification.

Similar analysis was carried out on Ni-20Cr samples corroded in LiCl-KCl to examine the role of Cr in corrosion. A STEM bright-field image and corresponding EDS mapping of the interface between Ni-20Cr and LiCl-KCl salt are shown in Fig. 4a. The Ni-20Cr alloy shows very fine grains at the surface as confirmed by the STEM bright-field image in Fig. 4a and the orientation mapping obtained by using the PED technique in TEM (see Fig. 4b). These fine grains were already present in as-received Ni-20Cr alloy before corrosion as shown in STEM bright-field image in Fig. S1 in supplementary information. The intergranular attack is evident from the STEM-BF indicated by the cyan colored arrows in Fig. 4a. The EDS maps of

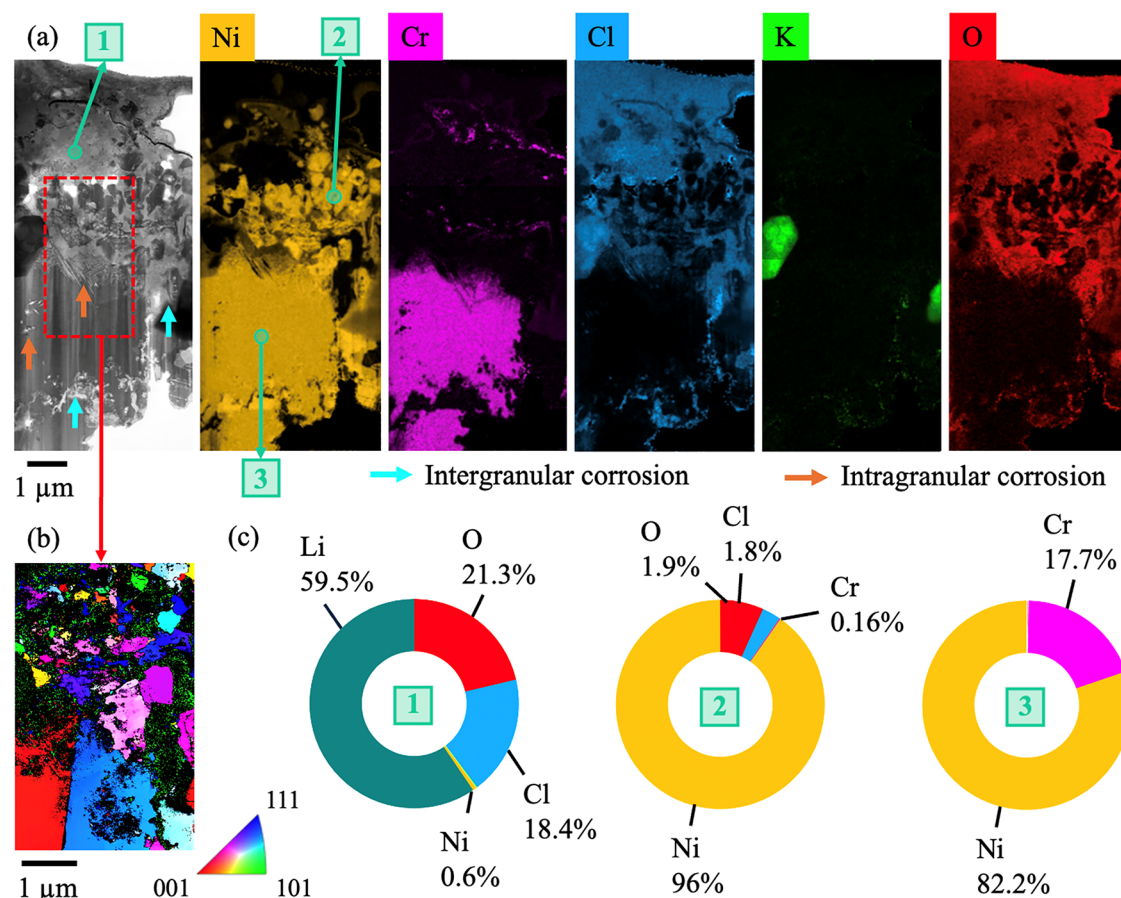


Fig. 5 | STEM-EDS-PED analysis of Ni-20Cr and LiCl-KCl-1wt%EuCl₃ salt interface. **a** STEM bright-field image and corresponding EDS maps of salt-alloy interface at low magnification, **(b)** PED orientation map of Ni-20Cr from dotted red

rectangle region in Fig. 6a, **(c)** EDS elemental composition analysis of region 1 (salt), 2 (Cr depleted Ni-20Cr alloy) and 3 (Ni-20Cr alloy).

Cl and K reveal salt penetration in the pore regions around the fine-grained surface region. The EDS mapping also revealed Cr depletion in the fine-grained surface region. The Cr loss was even stronger at the GBs (see inset image at the Cr map from the white dotted square region). This implies that the GBs were preferential diffusion pathways for Cr to selectively leach out in the molten salt. It is clear that all the corrosion features, including intergranular attack, salt penetration and Cr depletion, were limited around the fine-grained surface region (~2 μm from the surface), and there is no indication of damage in the larger bulk grains. Figure 4c shows EDS composition analysis from region 1 (salt near the interface), region 2 (larger bulk grains of Ni-20Cr alloy away from the salt-alloy interface), and region 3 (Cr depleted surface fine grains of Ni-20Cr alloy). The EDS elemental composition analysis of region 1 (salt) shows 50.4 at% Li, 22.9 at% Cl, 20.1 at% O and 5.2 at% Ni with small amounts of K (0.8 at%) and Cr (0.5 at%). Based on previous discussions, the smaller amount of K likely indicates a predominantly Li-rich salt. Interestingly, although the microstructural and microchemical features obtained from STEM-EDS suggest a stronger dissolution of Cr compared to Ni, the salt region near the interface is mostly rich in Ni rather than Cr (see Fig. 4c, EDS quantification of region 1). However, the ICP-MS analysis in section 3.2 does indicate that Cr dissolution in the bulk LiCl-KCl salt was approximately 360 times higher than that of Ni. The EDS elemental composition analysis of bulk grain (region 2) shows the expected 20.1 at% Cr, in contrast to the outer Cr depleted grains in (region 3) of Ni-20Cr alloy, which contain only 5.7 at% Cr, as shown in Fig. 4c.

Figure 5a shows a STEM bright-field image and corresponding EDS mapping of the interface between a Ni-20Cr sample and LiCl-KCl-1wt%EuCl₃ salt. EDS mapping shows Cr depletion in the outermost regions of the

sample. The corresponding PED orientation map in Fig. 5b shows fine grains in the outermost sample, but these grains are not attached to the larger bulk grains of Ni-20Cr alloy. This suggests that heavy GB attack and salt penetration caused the outer fine grains to detach and float in the salt near the interface. The EDS map of Cl suggests extensive salt penetration along GBs throughout the entire lamella (height ~10 μm). The cyan colored arrows in the STEM-BF image in Fig. 5a indicate regions of intergranular attack. The EDS maps of Cr and Ni also indicate significant Cr depletion and thereby Ni enrichment in the regions close to the GBs of larger bulk grains. This behavior is different from the Ni-20Cr corroded in blank LiCl-KCl, where the larger bulk grains were spared from corrosion attack (see Fig. 4). One notable feature observed after the corrosion of Ni-20Cr in LiCl-KCl-1wt%EuCl₃ was intragranular attack (see orange arrows in Fig. 5a). This behavior is discussed in detail in the following paragraphs.

EDS elemental composition analyses of different regions are shown in Fig. 5c. Region 1 represents Cl-rich salt, region 2 represents Cr-depleted floating fine grains, and region 3 represents larger bulk grains of the Ni-20Cr alloy. Region 1 shows enrichment of Li (59.5 at%), Cl (18.4 at%) and O (21.3 at%) with small concentrations of dissolved Ni (0.6 at%). However, the microstructure of Ni-20Cr after corrosion in LiCl-KCl-1wt%EuCl₃ indicates strong selective leaching of Cr and aggressive salt penetration deep into the material, the latter of which suggests significant dissolution of Ni. The ICP-MS results (Table 1) show significant amount of Cr and Ni in the LiCl-KCl-1wt%EuCl₃ salt after corrosion of the Ni-20Cr alloy. This result is consistent with the STEM-EDS analyses that indicate extensive localized corrosion of Ni-20Cr alloy in EuCl₃-containing salt. The STEM-EDS of the salt region at high magnifications are shown in Fig. 6 and are further discussed in the following paragraphs. Region 2 represents heavily Cr-depleted

outer fine grains. The EDS elemental composition analysis shows a majority of Ni and a negligible amount of Cr at 0.16 at%. The small concentrations of Cl and O may be due to the surrounding salt region, further confirming very strong Cr depletion in Ni-20Cr after corrosion in EuCl_3 -containing salt. Region 3 represents one of the larger grains of Ni-20Cr, showing a majority of Ni and 17.7 at% of Cr. This means some Cr depletion also occurred in the larger bulk grains of the Ni-20Cr alloy.

To further investigate the localized chemical environment near the interface, high-resolution imaging was performed on the salt region adjacent to Ni-20Cr. Figure 6a shows high-magnification STEM-BF images and the corresponding EDS mapping of the LiCl-KCl-1wt% EuCl_3 salt near the interface (region 1 of Fig. 5a). EDS mapping reveals various regions of interest in the salt labeled as regions 1, 2, 3 and 4. Figure 6b shows EDS elemental composition analysis of these regions. Region 1 is predominantly Ni-rich, with a concentration of 88.5 wt%. This suggests that these are likely breakaway grains of Ni-20Cr alloy that have lost almost all Cr due to selective leaching and significant amounts of Ni, which led them to shrink in size. The small concentration of Cl and O could indicate that the grains are embedded in the surrounding salt. Region 2 is also Ni-rich (46.9 wt%) but contains substantial amounts of Li (33.3 at%), Cl (11.1 at%), and O (24.1 at%) as well. Notably, this region contains negligible amounts of dissolved Cr. Region 3 is primarily rich in Li (57.4 at%), Cl (23.2 at%), and O (18.1 wt%), with negligible K, Cr, and

Ni, implying that it largely consists of LiCl and Li_2O . Lastly, region 4 is Cr-rich (19.8 at%) with significant amounts of Cl (26 at%), Ni (12.1 at%), and O (33.2 at%) as well.

To visualize the three-dimensional structure of corrosion pathways and elemental segregation at the interface, Fig. 7 shows 3D FIB-SEM-EDS tomography of the interface between LiCl-KCl-1wt% EuCl_3 and Ni-20Cr alloy. 3D EDS reconstructions of different elements of the salt region near the salt-alloy interface are shown in Fig. 7a. The phase separation of salt into K-rich and Li-, Ni-, and O-rich salt is evident from Fig. 7a. Cr is also present in certain areas within the salt, and its 3D morphology agrees well with the Cr STEM-EDS map shown in Fig. 6a. The 3D FIB-SEM tomography of salt/void interconnected network along the GBs in Ni-20Cr is shown in Fig. 7b. The single slice view SEM images in Fig. 7c also show corrosion attacks along GBs, twin boundaries (TBs) and triple junctions (TJs).

To further examine the intragranular corrosion features observed in Ni-20Cr after corrosion in LiCl-KCl-1wt% EuCl_3 , Fig. 8a, b present STEM-BF images and corresponding EDS mappings of the intragranular attack region in Ni-20Cr near the salt-alloy interface at low and high magnifications, respectively. Figure 8a reveals interesting directionality, indicating orientation dependence in both the Cr depletion pathways and subsequent salt penetration. Figure 8b confirms Cr depletion and salt penetration in channels that are 10–15 nm wide. Some channels exhibit only Cr depletion, while others show salt penetration to a certain depth followed by Cr depletion. The salt penetration suggests the dissolution of Ni in addition to Cr. Figure 8c shows EDS line scans on two channels, one showing Cr depletion and another showing salt penetration. The line scans indicate that Cr reaches approximately 1–3 at% in the channel. In the first channel, without salt penetration, Ni enriches to more than ~70 at%, while in the second channel with salt penetration, Ni goes below 50 at%. This indicates significant dissolution of Ni in the salt. It is also possible that the channels do not span the entire thickness of the TEM lamella.

To analyze the directionality of these intragranular attack channels, we aligned the larger Ni-20Cr grain with the [001] zone axis and acquired

Table 1 | ICP-MS analysis of salt composition after corrosion (units: ppm (10^{-4} wt%))

Sample	Salt	Composition	
		Ni	Cr
Ni	LiCl-KCl	0.048 ± 0.002	-
	LiCl-KCl-1wt% EuCl_3	39.8 ± 1.4	-
Ni-20Cr	LiCl-KCl	0.036 ± 0.001	12.8 ± 0.4
	LiCl-KCl-1wt% EuCl_3	22.8 ± 0.8	497 ± 15.7

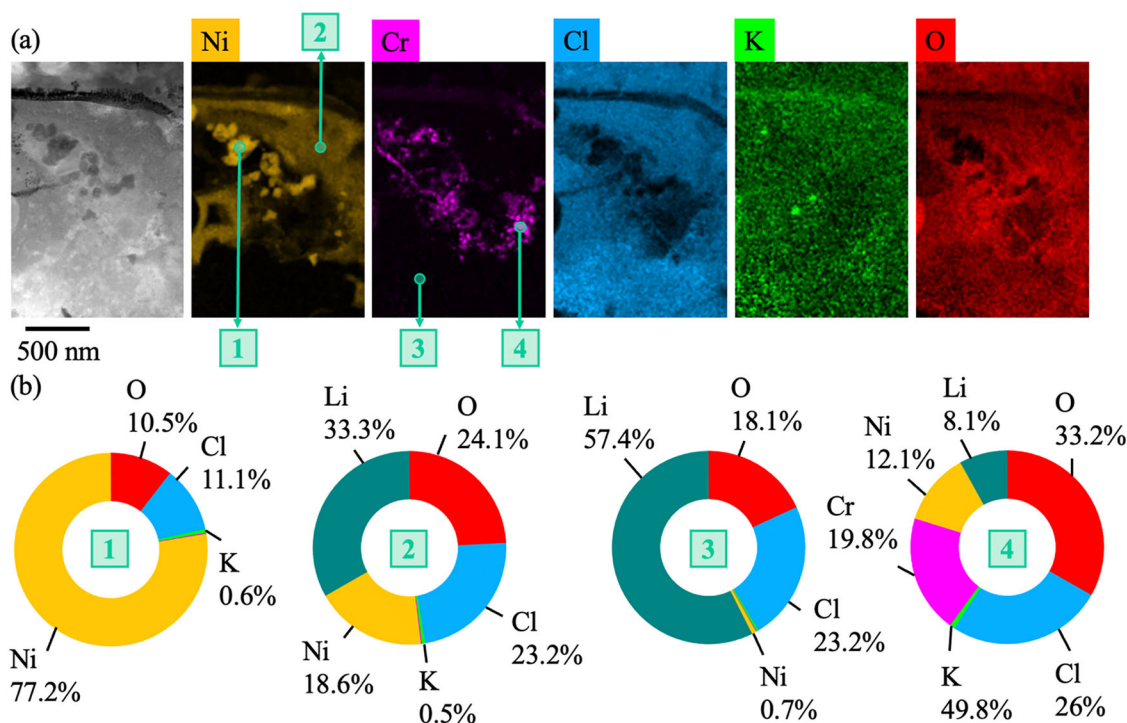


Fig. 6 | High-magnification STEM-EDS analysis of the LiCl-KCl-1wt% EuCl_3 salt. a High-magnification STEM bright-field image and corresponding EDS maps of LiCl-KCl-1wt% EuCl_3 salt, **(b)** EDS elemental composition analysis of different regions of interests.

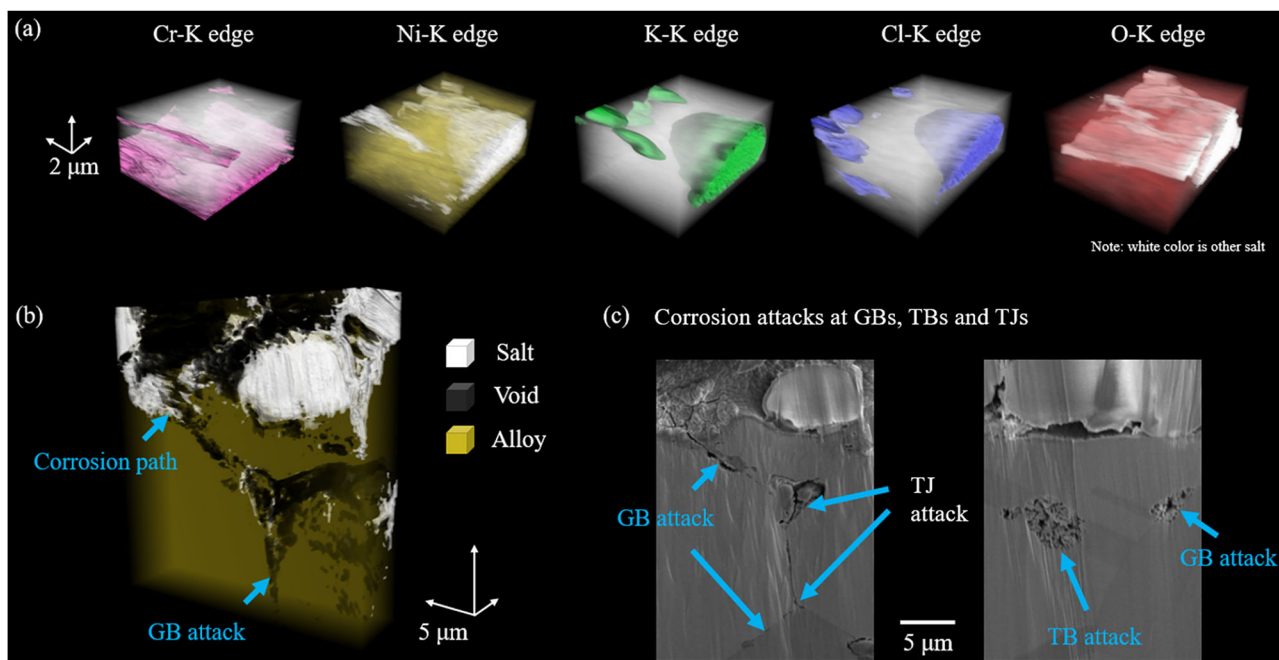


Fig. 7 | 3D FIB-SEM-EDS tomography of the interface between LiCl-KCl-1wt% EuCl_3 and Ni-20Cr alloy. a 3D elemental reconstructions showing phase separation in the salt and distribution of key elements near the interface, and (b) 3D

morphology of a larger volume showing surface salt and GB attack in Ni-20Cr alloy. c Single-slice SEM images highlighting extensive corrosion attacks at GBs, TBs and TJs.

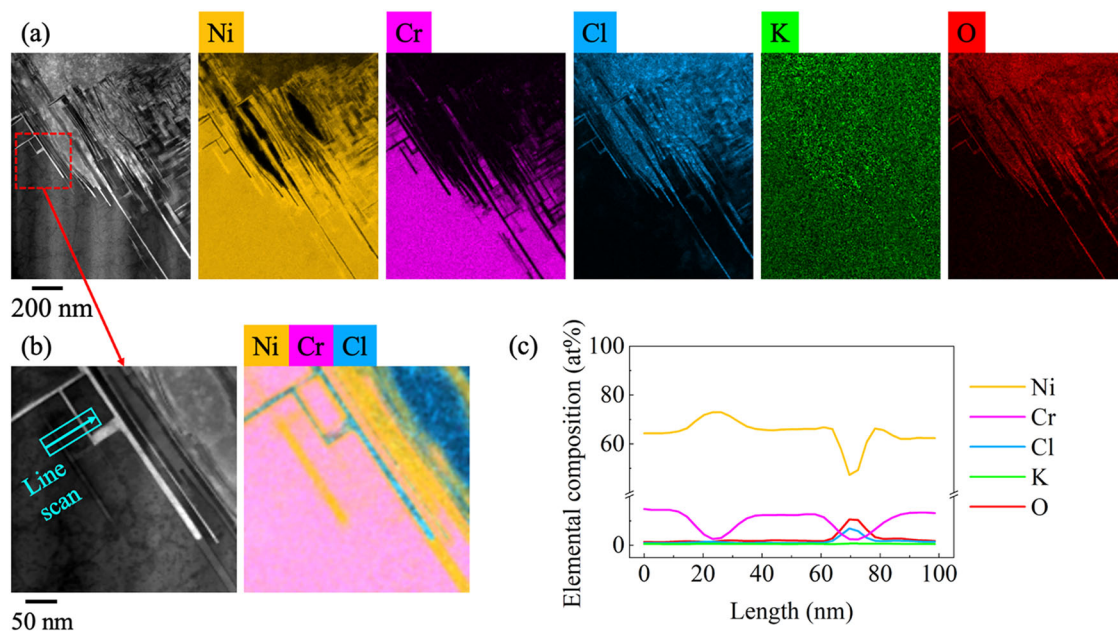


Fig. 8 | STEM-EDS analysis of the intragranular attack region of Ni-20Cr. STEM bright-field images and corresponding EDS maps near the salt-alloy interface at (a) low and (b) high magnifications, (c) EDS line scans along intragranular corrosion channels.

STEM-BF images. The low-magnification on-zone STEM-BF overview image in Fig. 9a shows different intragranular corrosion regions. Figure 9b, c show the high-magnification images of the regions denoted by cyan and yellow dashed squares in Fig. 9a. The selected area diffraction pattern (SADP) and corresponding stereographic projections are shown in Fig. 9d, e. The stereographic projection shows the orientation of different crystallographic planes. From Fig. 9b, c, it is evident that Cr depletion and salt penetration occurred preferentially along the {001} family of crystallographic planes in the FCC lattice of the Ni-20Cr alloy.

Chemical reactions during corrosion

Corrosion in molten salts is a complex process where the rates of chemical reactions and elemental diffusion in surfaces/interfaces, in molten salts and in structural materials play a significant role in determining the extent and the nature of damage^{16,21,29,31,35–37}. In this work, the combination of in situ optical spectroscopy, ICP-MS, and electron microscopy techniques was used to gain insights into the governing mechanisms behind the chemical evolution of salts and the microstructural evolution of pure Ni and Ni-20Cr model alloy during molten salt corrosion in the presence of highly oxidizing

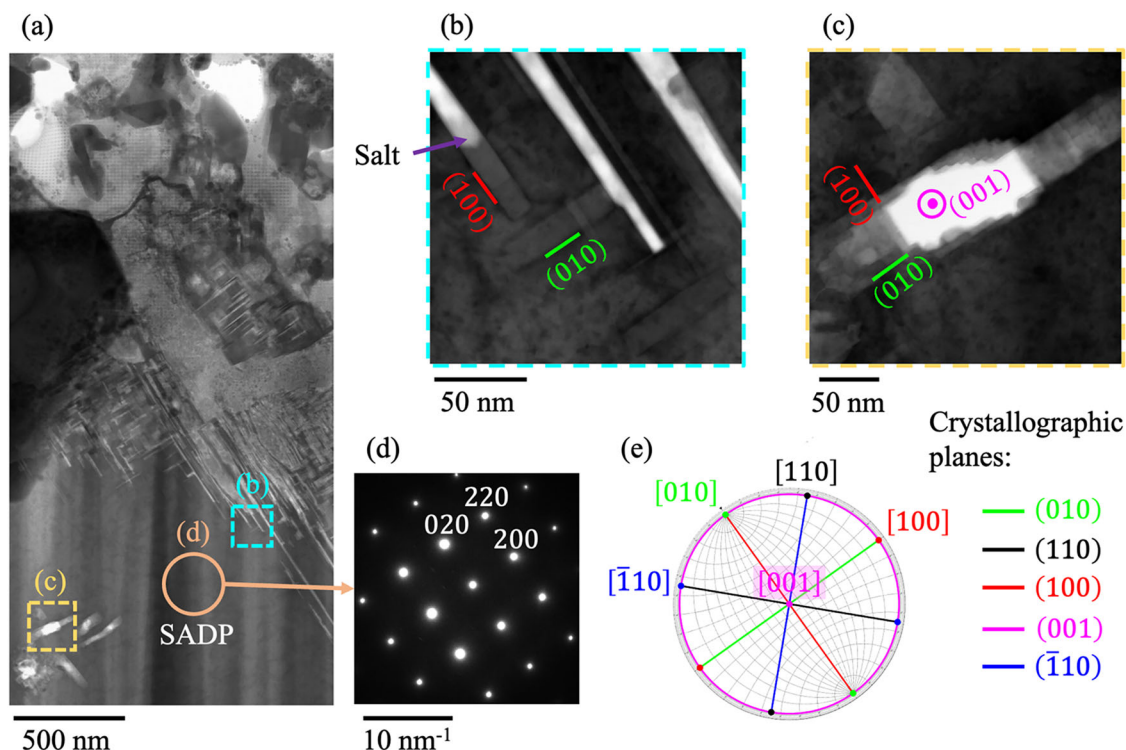
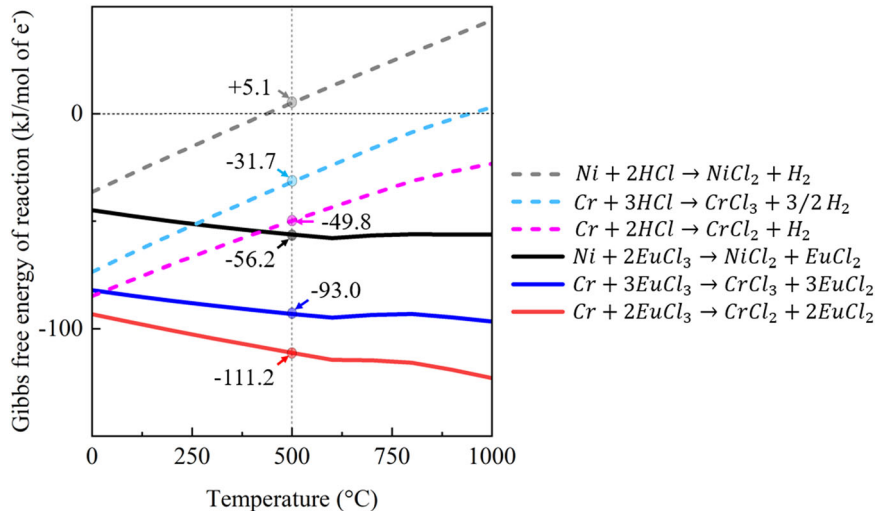


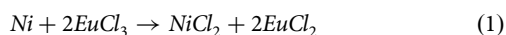
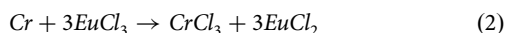
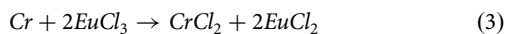
Fig. 9 | On-zone STEM imaging and diffraction analysis of Ni-20Cr corroded in LiCl-KCl-1wt%EuCl₃. **a** Low magnification STEM bright-field image of the salt-alloy interface showing an intragranular corrosion region, **(b, c)** high-magnification STEM bright-field images of intragranular corrosion regions denoted by dotted cyan

and yellow squares in **(a, d)** selected area diffraction pattern (SADP) from Ni-20Cr alloy region, **(e)** corresponding stereographic projection showing orientations of different planes.

Fig. 10 | Gibbs free energy of reaction (ΔG_{rxn}) for the relevant reactions (normalized as kJ/mol of e^- transferred) studied in this work.



EuCl₃. The reactions by which EuCl₃ oxidize alloying elements like Ni and Cr while reducing itself to EuCl₂ are expressed as follows:

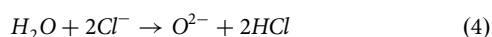


To better understand the thermodynamic driving forces behind the observed corrosion behavior, we evaluated the Gibbs free energies of these relevant redox reactions (normalized as kJ/mol of e^- transferred). Figure 10

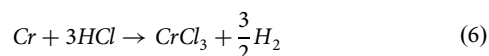
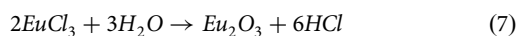
shows the Gibbs free energy of these reactions (ΔG_{rxn}) obtained using HSC Chemistry software³⁸. In the context of the reactions between Cr and EuCl₃, the ΔG_{rxn} values are more negative, which indicates a higher thermodynamic tendency for chromium to dissolve during corrosion. It must be noted that, although Ni is more noble than Cr in the presence of EuCl₃, its ΔG_{rxn} values are still negative, indicating that the reaction is spontaneous (see Fig. 10). This means that Cr and Ni dissolution is thermodynamically spontaneous in the presence of EuCl₃, with Cr showing a higher tendency to dissolve, consistent with its more negative ΔG_{rxn} values. This is evident in the ICP-MS measurements, where significant Ni dissolution was seen after corrosion of Ni and Ni-20Cr in EuCl₃-containing salt. Moreover, Cr dissolution from Ni-20Cr wire after corrosion in LiCl-KCl-1wt%EuCl₃ was

considerably higher (~ 22 times) than the amount of dissolved Ni, consistent with the calculated thermodynamic driving forces. However, thermodynamic driving forces alone cannot account for the dramatically enhanced dissolution rates in EuCl_3 -containing salt compared to blank LiCl-KCl. The $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox couple is fast and reversible in LiCl-KCl^{33,34}, facilitating rapid electron transfer at the metal surface and thereby significantly lowering the activation barrier for Ni and Cr dissolution. EuCl_3 is therefore the primary oxidant driving accelerated corrosion in EuCl_3 -containing salt.

It is worth noting that corrosion progresses in the blank LiCl-KCl as well, even if it is to a much smaller extent as compared to that in EuCl_3 -containing salt. The corrosion experiments and subsequent characterization in this paper were conducted in a manner that the exposure to air and moisture was kept as low as possible, but the cuvette was still open to the glovebox atmosphere. It is well known that chloride salts are extremely hygroscopic so the presence of trace amounts of residual moisture in the salt cannot be ruled out. Accordingly, the STEM-EDS and FIB-EDS tomography results clearly indicate the considerable presence of oxygen near the salt-material interface in all samples. In the molten chlorides, the residual moisture can dissociate to form oxygen ions and HCl by the following reaction^{39,40}:



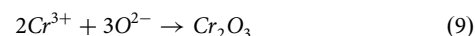
Previous studies have shown that the presence of even very small amounts of moisture in molten chloride salts can lead to the formation of HCl and dramatically increase corrosion rates of structural alloys (by 1–2 orders of magnitude)^{10,35,41,42}. The primary oxidant that drives the corrosion in the absence of EuCl_3 is actually HCl, according to reactions (5–6) listed below.



We compared ΔG_{rxn} values at 500 °C for HCl and EuCl_3 -driven oxidation reactions (see Fig. 10). Although HCl-driven Ni dissolution is slightly positive at 500 °C ($\Delta G_{\text{rxn}} = +5.1 \text{ kJ/mol of } e^-$) the H_2 generated by the reaction can continuously escape from the molten salt. The resulting decrease in H_2 activity shifts the reaction equilibrium toward the products, allowing a limited amount of Ni dissolution to be seen during corrosion in blank LiCl-KCl. The HCl-driven Cr dissolution remains spontaneous, consistent with the small but measurable Cr content in the salt after corrosion. EuCl_3 itself is also very stable in the presence of moisture. The ΔG_{rxn} of the possible reaction between EuCl_3 and moisture (see reaction (7)) is positive ($\Delta G_{\text{rxn}} = +42.1 \text{ kJ/mol}$), making it thermodynamically unfavorable. EuCl_3 therefore dominates corrosion through the combination of sufficient thermodynamic driving force, high concentration (1 wt%), and fast electron transfer kinetics via the $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox couple^{33,34}.

The chemical analysis of the interfacial salt using EDS clearly reveals that oxygen is mainly collocated with Ni and Li-rich regions of salt after solidification. The presence of Ni^{2+} peaks during in situ optical spectroscopy measurements with both pure Ni and Ni-20Cr alloy wires in LiCl-KCl-1wt% EuCl_3 salt means that Ni dissolves as a soluble product. The anodic reaction involving dissolution of Ni to Ni^{2+} ions in the molten salt as expressed in reaction (5) for blank LiCl-KCl and reaction (1) in the case of EuCl_3 -containing salt. These Ni^{2+} ions can react with O^{2-} ions to form insoluble NiO as shown in reaction (8). Depending on local changes in the oxygen potential due to the consumption of O^{2-} , the reaction (8) can reverse itself to form Ni^{2+} ions again^{42,43}. This means that the resulting Ni-rich corrosion product can be a mixture of soluble Ni^{2+} ions and insoluble NiO that are in equilibrium. STEM-EDS results of all samples show Li, Ni, O, and

Cl-rich salt regions, which are likely to be a mixture of oxides/oxychlorides of Li and Ni. We couldn't identify these compounds using the current results. It is interesting to note that K-rich salt regions show negligible Ni, meaning most Ni ions partition to Li-rich corrosion products. The STEM-EDS-EELS results of Ni-20Cr corroded in LiCl-KCl-1wt% EuCl_3 , show Cr in the oxide form (Fig. 6), Cr_2O_3 as per reaction (9). It is thermodynamically favorable for Cr_2O_3 to form at a much smaller oxygen potential than NiO ⁴³. The solubility of Cr_2O_3 in molten chloride salts is very low (~ 0.1 wt% at 727 °C in NaCl-KCl⁴⁴), and expected to be lower still at 500 °C. Consequently, Cr^{3+} ions precipitate rapidly as insoluble Cr_2O_3 particles rather than remaining as dissolved ionic species, explaining the absence of $\text{Cr}^{2+}/\text{Cr}^{3+}$ peaks in optical spectra. These particles migrate into bulk salt, consistent with Fig. 6 (Region 4), and are captured by ICP-MS acid digestion, reconciling the apparent discrepancy between the three characterization techniques. Guo et al.³², have shown oxide products forming as powders away from the salt-material interface. Although EuCl_3 is a primary oxidant in EuCl_3 -containing salt, the presence of moisture still plays an important role in the formation of corrosion products.



Planar and intergranular corrosion of Ni

Microstructural evolution can be better visualized using the schematic representation shown in Fig. 11a–d. In pure Ni, the corrosion manifests mainly as shallow intergranular cracks in both molten LiCl-KCl and LiCl-KCl-1wt% EuCl_3 . The GB attack can be attributed to their higher free energies as compared to the bulk, which makes them thermodynamically more susceptible to corrosion. The in situ optical spectroscopy and ICP-MS measurements clearly indicate much higher dissolution of Ni in LiCl-KCl-1wt% EuCl_3 as compared to LiCl-KCl. This means the intergranular corrosion rate is only slightly higher than the planar corrosion rate. At the surface, the area of the grain interior exposed to the molten salt is clearly higher than that of the near-GB region. This means that most dissolved Ni erodes from the surface of exposed grain interiors, as shown by double arrows Fig. 11a, b, suggesting a dominant planar corrosion front.

Pure Ni coatings are amongst one of the alternatives to mitigate corrosion of structural alloys exposed to molten salts. Ni-coated alloys have shown 1–2 orders of magnitude improvement in molten salt corrosion resistance depending on the processing techniques, microstructures and thicknesses of coatings^{45–50}. Bhavé et al.⁴⁷ used phase field simulations to study the effectiveness of Ni coatings on Ni-Cr alloys. The corrosion resistance of Ni coating was attributed to the decrease in fast diffusion paths for Cr along the coating GBs. They show that lower susceptibility to localized corrosion in pure Ni can be beneficial to mitigate molten salt corrosion damage. However, our results indicate that rapid dissolution of Ni in the presence of strongly oxidizing additives like EuCl_3 still cannot be avoided.

Intergranular corrosion of Ni-20Cr

In Ni-20Cr alloy, localized corrosion seems significantly more dominant compared to planar corrosion, as shown in Fig. 11c and d. In both LiCl-KCl and LiCl-KCl-1wt% EuCl_3 , corrosion initiates primarily with Cr depletion in the near-GB regions, followed by Ni dissolution and salt penetration. The severity of corrosion is markedly higher in LiCl-KCl-1wt% EuCl_3 than LiCl-KCl, with GB attack extending deep into the material, far beyond the salt-material interface. The selective dissolution of Cr over Ni is consistent with thermodynamic predictions for molten salt systems^{10,11,29,51–54}. To understand this process better, we also estimated self-diffusion (D_S) and grain boundary diffusion coefficients (D_{GB}) of both Cr and Ni elements in Ni-20Cr alloy using the data available in Moulin et al.'s paper⁵⁵. The diffusion coefficient of Cr in bulk ($D_S^{\text{Cr}} = 1.0 \times 10^{-22} \text{ m}^2/\text{s}$) is 8 orders of magnitude slower than in GBs ($D_{GB}^{\text{Cr}} = 1.9 \times 10^{-14} \text{ m}^2/\text{s}$ when GB width is 0.5 nm). It should be noted that bulk diffusion involved in Cr loss is highly non-

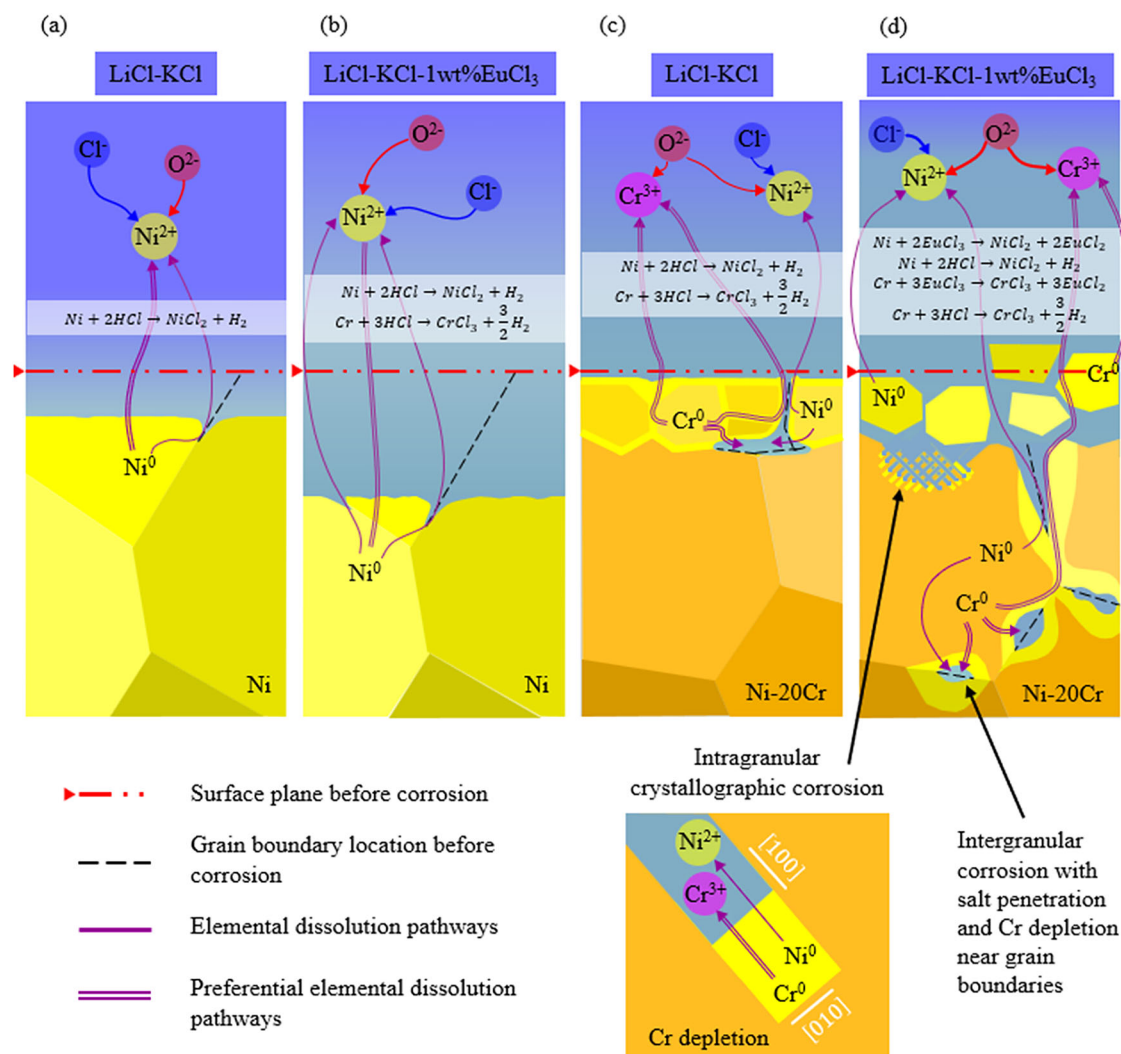


Fig. 11 | Schematic diagram depicting corrosion mechanisms in Ni and Ni-20Cr exposed to LiCl-KCl with and without 1 wt% EuCl₃. a Ni in LiCl-KCl, **(b)** Ni in LiCl-KCl-1wt%EuCl₃, **(c)** Ni-20Cr in LiCl-KCl, and **(d)** Ni-20Cr in LiCl-KCl-1wt%EuCl₃.

equilibrium, but it is unlikely to surpass an 8-order-of-magnitude difference. Similarly, the diffusion coefficient of Ni in bulk ($D_S^{\text{Ni}} = 4.7 \times 10^{-23} \text{ m}^2/\text{s}$) is 6 orders of magnitude slower than in GBs ($D_{\text{GB}}^{\text{Ni}} = 4.5 \times 10^{-17} \text{ m}^2/\text{s}$ when GB width is 0.5 nm). This means Cr diffuses fast along GBs outward toward the salt interface, where it is consumed by dissolution as $\text{CrCl}_2/\text{CrCl}_3$. The preference for intergranular corrosion can be attributed to the selective dissolution of Cr along fast diffusion pathways like GBs^{52,56}. However, the bulk diffusion of Cr from grain interiors toward the GBs is too slow at 500 °C to replenish the Cr being lost along these short-circuit paths. This creates a vacancy-rich, Cr-depleted zone immediately adjacent to the boundary because Cr has left lattice sites faster than bulk transport can refill them. Ni atoms, being mobile along the same short-circuit GB paths and through the bulk at 500 °C can partially fill some of those vacant sites. However, Ni is also being consumed by corrosion as NiCl_2 , especially in EuCl_3 -containing salt, where it is thermodynamically favored, albeit to a lesser extent than Cr (see Fig. 10). The near-GB regions supersaturated with vacancies can condense into stable voids. These voids are interconnected along the boundary network and become accessible to the molten salt, which wets them readily^{10,11,29,52,54,57}. This is evident from the 3D FIB-SEM-EDS results in Fig. 7c. In addition to GBs, corrosion attacks also occurred along TBs and TJs (see Fig. 7c).

It is surprising that although ICP-MS studies showed significant dissolution of Cr, STEM-EDS studies suggest that its occurrence near the salt-alloy interface and within pores was limited as compared to dissolved Ni. Cr

dissolution likely occurs earlier and faster than Ni. Cr ions diffuse within the salt away from the interface in search of oxygen and form oxides, leading to sparse occurrence of Cr-rich oxides (see Fig. 6) in the interfacial STEM-EDS results but relatively higher concentrations of Cr in ICP-MS analysis of bulk salt after corrosion. The significant number of Ni-rich regions in the salt near the interface can be attributed to dissolution from largely Cr-depleted and Ni-rich interfacial alloy regions. Mills et al.⁵⁴ reported the formation of interconnected salt-filled pores in Ni-20Cr after corrosion in molten LiF-NaF-KF (FLiNaK) salt with EuF_3 as an additive. These interconnected pores showed Cr-rich layers at salt-alloy interfaces, which were attributed to time-dependent lattice diffusion of elements from alloy to pore surface to maintain a Cr-rich surface that is energetically favorable compared to a Ni-rich surface facing the salt⁵⁴. In this study, we mainly observed Ni-rich surfaces facing salt after corrosion. This means that the fundamental corrosion processes in molten salts are extremely complex and influenced by multiple factors, such as the thermodynamics of salt-alloy interfaces, mass transport of both elements within the alloy and salt after dissolution, and need to be studied systematically using clever experimental and modeling techniques in the future.

Intragranular crystallographic corrosion of Ni-20Cr

The STEM-EDS images of Ni-20Cr corroded in LiCl-KCl-1wt%EuCl₃ also showed a very interesting type of intragranular crystallographic corrosion where dissolution of Cr and then followed by Ni occurred along different

variants of {100} planes (see the magnified schematic of intragranular corrosion region in Fig. 11d). The crystallographic corrosion has been reported before. Guo et al.³² work on EuCl_3 -induced corrosion of Inconel 718 Ni-based superalloy in LiCl-KCl molten salt also showed multiple intragranular cracks seemingly originating from existing intergranular cracks in different grains, but did not explain the reasons. Chan et al.³⁷, studied corrosion of pure Cr in molten FLiNaK salt with different electrochemistry techniques under open circuit as well as different applied potentials. A faceted microstructure, indicative of crystallographic attack, was observed after corrosion when the corrosion rate was controlled by charge transfer processes as opposed to salt-film-mediated mass-transport regimes³⁷. Our previous work on quasi in situ TEM of Ni-20Cr TEM disc sample showed single intragranular (i.e., transgranular) cracking after corrosion in molten KCl-MgCl₂ salt. Recently, Evered et al.⁵⁸ observed faceted morphology along {100} family of planes in 316 stainless steel samples after exposure to molten FLiNaK salt. It was attributed to preferential adsorption of F⁻ ions on {100} family of planes which acted as corrosion site blockers and effectively increased the activation energy of corrosion reactions. The crystallographic corrosion behavior in the form of transgranular non-slip plane microcleavage behavior has been observed during stress corrosion cracking in aqueous environments. Zhu et al.⁵⁹, proposed a cleavage dissolution model to explain preferential brittle rupture along low surface energy {100} planes with synergistic anodic dissolution of crack fronts in 316 L stainless steel exposed to boiling MgCl₂ solution. The low surface energy of {100} was attributed to synergistic adsorption of H and Cl atoms in the octahedral interstices of {100} planes.

We utilized DFT methods to calculate surface energies of (100), (110), and (111) planes in Ni-20Cr. The surface energies of the three crystallographic planes were calculated for all surface terminations. After relaxing all the structures and calculating the surface energies, it was found that, depending on the surface terminations, there was a range of possible energies for each crystallographic direction. For the twenty different terminations possible in the (100) surfaces, the surface energy varied between 2.32 J/m² and 2.52 J/m². In this case of the (110) surfaces, the surface energies varied between 2.49 J/m² and 2.67 J/m², while for the (111) surfaces, the surface energy ranged from 2.11 J/m² to 2.30 J/m². Comparing the surface energies the order of increasing surface energy, and therefore decreasing stability of the surfaces, is determined to be {111} < {100} < {110}.

When there is ongoing dissolution in a concave geometry (as in the experiment), it is expected that slow facets appear and persist in accordance with the kinetic Wulff shape construction^{60,61}. Thus, kinetically, the appearance of the {100} facet at the corrosion front would be explained if it is most stable against corrosion. Our DFT calculations show the full vacuum phase ordering as {111} < {100} < {110}. By this ordering alone {111} should be the least corrosion-susceptible surface, a prediction consistent with Arkoub et al.'s⁶² ReaxFF-MD study of Ni-25Cr alloy exposed to molten FLiNaK salt. Yet this is not what we observe: neither in our experiments nor the literature shows {111} as the least corrosion-susceptible surface. In fact, the cross-section of channel walls in Fig. 9c showed facets/terraces with {100} orientation, indicating that the {100}-oriented channel walls have the lowest interfacial energy.

Sun et al.⁶³ showed that local Cr content at the surface of Ni-12Cr alloys can alter the vacuum surface-energy ordering: varying the near-surface concentration shifts the ordering from {111} < {100} < {110} at zero Cr to {110} < {111} < {100} at full Cr coverage. This clearly indicates that the surface energy ordering is dependent on local Cr content. However, across the range of surface Cr contents examined, Sun et al.⁶³ never identified {100} as the lowest energy surface, so Cr depletion alone does not fully account for why {100} is preferentially selected. These results indicate that vacuum surface energy is not the governing descriptor of corrosion susceptibility in this system, but rather the salt-alloy interfacial energy and/or kinetic stability (not thermodynamic stability), which need not follow the same ranking, are likely the more relevant parameters. For example, greater anion adsorption may lead to lower interfacial energy or allow molten salt to penetrate the

surface layer, thereby increasing the corrosion rate^{62,64}. The experimental observation of {100}-oriented channel walls thus confirms the thermodynamic stability (i.e., low interfacial energy) and kinetics stability (i.e., the low corrosion rate) of the {100} facets.

We are the first to report such deep, narrow channel intragranular crystallographic corrosion morphology after molten salt exposure. It is worth noting that the mechanisms presented here are speculative because the metal-salt interfacial energies, orientation-specific anion adsorption behavior, or the facet-resolved dissolution kinetics are not known for this specific alloy-salt system. This remains an open question and will require extensive combined experimental and computational research work in the future.

Summary

This paper investigated the effects of EuCl_3 addition in the molten LiCl-KCl salt on the corrosion mechanisms of pure Ni and Ni-20Cr model alloy using novel in situ optical spectroscopy, post-corrosion ICP-MS chemical analysis of salt, and electron microscopy analysis of salt-material interface. The molten LiCl-KCl-1wt% EuCl_3 salt was found to be extremely corrosive for both pure Ni and Ni-20Cr alloy and caused accelerated dissolution of Ni and Cr as compared to blank LiCl-KCl. In both Ni and Ni-20Cr, significant dissolution of Ni in the form of Ni^{2+} ions was confirmed using in situ optical spectroscopy measurements when exposed to EuCl_3 -containing molten salt. The post-corrosion ICP-MS chemical analysis of the salt showed an 800-fold increase in Ni dissolution in pure Ni and 600- and 22-fold increases in the dissolution of Ni and Cr from Ni-20Cr alloy, respectively, due to the addition of EuCl_3 in salt.

In pure Ni, the microstructure showed the presence of shallow cracks along the GBs after corrosion in both LiCl-KCl and LiCl-KCl-1wt% EuCl_3 . This is because corrosion was dominated by planar dissolution of Ni with occasional localized attacks at the GBs. In the Ni-20Cr alloy, the microstructure was strongly dominated by localized intergranular attack with selective leaching of Cr in both LiCl-KCl and LiCl-KCl-1wt% EuCl_3 . The extent of corrosion attack was very severe in the Ni-20Cr sample corroded in the LiCl-KCl-1wt% EuCl_3 salt, with intergranular corrosion accompanied by pore formation, salt penetration, and extensive Cr depletion along the GBs. This paper also uncovered a unique intragranular corrosion mechanism in Ni-20Cr when exposed to EuCl_3 -containing salt. The intragranular attack manifested in the form of small channels (~10–15 nm width, several microns in length and height) with salt penetration along different variants of {100} crystallographic planes. This behavior was attributed to thermodynamic and kinetic stability of {100} crystallographic planes under molten salt attack.

Methods

In situ optical spectroscopy

Drawn wire samples (diameter = 1 mm, length = 10 mm) of pure Ni and Ni-20Cr model alloy were procured from Alfa Aesar and used as received. Anhydrous LiCl-KCl eutectic (99.99% purity, trace metals basis), EuCl_3 (99.99% purity, trace metals basis), NiCl_2 (99.99% purity, anhydrous), CrCl_2 (99.99% purity, anhydrous), CrCl_3 (99.99% purity, anhydrous) were sourced from Sigma-Aldrich and used as received. All procedures involving salt handling and in situ optical spectroscopy measurements were conducted within an argon-filled glovebox (Vacuum Technologies Inc.), maintaining oxygen and moisture levels below 0.1 ppm. Figure 12a shows a schematic representation of the in situ optical spectroscopy corrosion experimental setup. We utilized a Cary 5000 spectrophotometer, outfitted with deuterium and tungsten lamps to enable coverage across the ultraviolet-visible-near infrared spectrum from 200 to 2300 nm. High-temperature fiber optic cables, rated for up to 700 °C and sourced from Fiberguide, Inc., connected the externally located spectrophotometer to a custom high-temperature spectroscopy furnace housed inside the glovebox. Molten salt samples were placed in a 1 cm optical pathlength quartz cuvette placed on a graphite-constructed multi-cell rack to capture absorption spectra in transmission mode. Further intricacies of our high-temperature

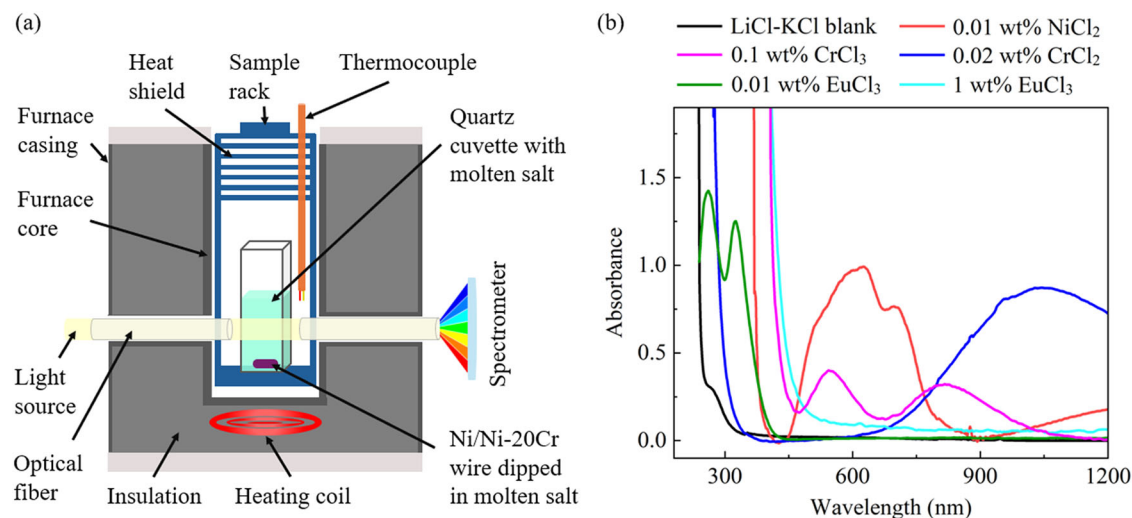


Fig. 12 | In-situ optical spectroscopy experimental setup and optical absorption spectra of standards. **a** Schematic representation of the in situ optical spectroscopy corrosion experimental setup⁶⁵, **b** Optical absorption spectra of Ni^{2+} , Cr^{2+} , Cr^{3+} and Eu^{3+} standards in LiCl-KCl eutectic.

spectroscopy system are described elsewhere⁶⁵. To ensure accuracy, the wavelength calibration of the spectrophotometer, from 280 to 880 nm, was validated using a NIST-certified didymium perchlorate reference material. This aqueous solution is sealed in a high-grade far-UV quartz cell, with certificate number 72641.

Prior to use, quartz cuvettes were cleaned with isopropanol and vacuum-dried at 125 °C overnight, along with custom quartz lids designed to minimize salt volatilization at elevated temperatures. Each cleaned cuvette was loaded with 5 g of LiCl-KCl eutectic salt and equilibrated at 500 °C to establish a baseline spectrum (black spectrum, Fig. 12b). To obtain reference optical spectra, LiCl-KCl was doped individually with 0.01 wt% NiCl_2 , 0.1 wt% CrCl_3 , 0.02 wt% CrCl_2 , 0.01 wt% EuCl_3 and 1 wt% EuCl_3 . After two hours of melting at 500 °C for homogeneity, distinct optical signatures were recorded for each chloride: NiCl_2 (400–800 nm, red), CrCl_3 (450–1100 nm, pink), CrCl_2 (600–1400 nm, blue) and EuCl_3 (200–400 nm, green), as shown in Fig. 12b. A spectrum corresponding to 1 wt% EuCl_3 in LiCl-KCl (cyan curve, Fig. 12b), referred to as LiCl-KCl-1wt% EuCl_3 throughout this work, shows saturated EuCl_3 peaks in the UV region. Importantly, in case of 1 wt% EuCl_3 , the visible and near IR range (400–1200 nm) remains spectrally clear, ensuring clear identification of NiCl_2 and $\text{CrCl}_3/\text{CrCl}_2$ species. Ni wires were introduced into two separate cuvettes containing molten LiCl-KCl, one loaded with 1 wt% EuCl_3 and one without EuCl_3 , to compare corrosion behavior in the presence and absence of the oxidizing agent. Ni-20Cr wires were tested in a similar manner. The concentration of 1 wt% EuCl_3 was selected to provide sufficient oxidant to drive measurable dissolution of Ni and Cr while maintaining Ni^{2+} concentrations within the linear detection range of the spectrophotometer. As shown in Fig. 12b, at this concentration EuCl_3 saturates only the UV region (200–400 nm), leaving the 400–1200 nm window spectrally clear for unambiguous identification of Ni^{2+} and $\text{CrCl}_2/\text{CrCl}_3$ species. This concentration is also comparable to the 2 wt% EuCl_3 used by Chang et al.²⁵, where EuCl_3 was added to increase the corrosion driving force to observable levels over short test durations. In situ optical spectra were collected in cyclic mode every 4 minutes during the corrosion test, with a total of 40 and 60 cycles (160 and 240 minutes) for Ni and Ni-20Cr, respectively, in both salt conditions.

Post-corrosion characterization

After in situ optical spectroscopy experiments, the salt was allowed to cool to room temperature under an argon inert atmosphere and the Ni and Ni-20Cr wires were retrieved inside the glovebox. The salt was ground and analyzed for chemical composition using an ICP-MS technique (Agilent

7900). Approximately 0.5 g of the salt sample was dissolved in 10 mL of trace metal grade HNO_3 and diluted with ultrapure water (18.2 M Ω /cm). A range of quality assurance/quality control (QA/QC) measures were implemented to ensure the validity of the results, including blanks, duplicates, independent calibration verifications (ICV), and sample spikes, all of which met acceptance criteria ($\pm 10\%$ for blanks and duplicates; $\pm 15\%$ for sample spikes).

The Ni and Ni-20Cr wires were intentionally left with some residual salt on their surface for cross section analysis. The TEM lamellae were prepared from both Ni and Ni-20Cr wires using in situ lift-out technique in FIB-SEM instrument (FEI Quanta Dual beam) at the Center for Advanced Energy Studies (CAES) at Idaho National Laboratory (INL). The STEM-EDS-EELS analysis was conducted using a Thermo Scientific Titan Themis 200 TEM equipped with Super-X EDS, Gatan Continuum ER EELS. It is important to note that EDS cannot quantify lithium. We utilized the principle of charge neutrality to estimate the concentration of Li^+ ions to compensate for the molar excess of anionic O^{2-} and Cl^- over cationic Ni^{2+} , Cr^{3+} and K^+ detected by EDS. The grain orientation mapping was performed using the PED technique using a Nanomegas ASTAR system in the Thermo Scientific Spectra 300 TEM.

Additionally, the samples were analyzed by 3D FIB-EDS tomography using a Thermo Scientific Helios G4 multibeam plasma FIB instrument using serial sectioning technique. We collected two consecutive frames every ~200 nm, one at 5 kV to reveal grain contrast and another at 30 kV for getting high EDS counts, yielding two corresponding sets of SEM-EDS images. The Fast Fourier transform (FFT) method was employed to align the SEM and EDS images. The aligned stack of SEM and EDS images was then smoothed and cropped using the Median (3D) plugin and the Crop3D routine in the FIJI package of ImageJ⁶⁶. Thresholding segmentation was performed on the SEM images to differentiate the void, light elements (Li and K) and heavy elements (Ni and Cr) regions. Thresholding segmentation was also used to differentiate the target element regions on the EDS image stacks. The processed image stacks were then visualized in 3D using the software Tomviz⁶⁷.

Surface energy calculations using DFT

The surface energies of the three lower Miller index surfaces (100), (110), and (111) of Ni-20Cr were calculated using density functional theory (DFT)^{68,69}. All DFT calculations were performed using the projected augmented wave (PAW) method⁷⁰ within the Vienna Ab-initio Simulation Package (VASP)⁷¹, employing the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) functional⁷² for

exchange and correlation. The Ni-20Cr system has a face-centered cubic structure, and the chemical disorder was simulated using the special quasi-random structure (SQS)⁷³ as implemented in the Alloy Theoretic Automated Toolkit (ATAT) software package⁷⁴. A supercell consisting of 100 atoms (80 Ni atoms and 20 Cr atoms) was created using the SQS method, and the bulk structure was subjected to geometric optimization while maintaining the cubic geometry, with an energy cutoff of 400 eV (higher than the recommended cutoff value) and a k-point mesh of $2 \times 2 \times 2$. The convergence criteria for the total energy were set to 1×10^{-6} eV. The Methfessel-Paxton smearing method⁷⁵ was employed for partial occupancies, with a sigma value of 0.2 eV. After the Ni-20Cr bulk system was fully optimized, different surface structures corresponding to the (100), (110), and (111) planes were created using the Pymatgen software package⁷⁶. A periodic slab model was used to calculate the surface energy, and a vacuum of 15 Å was introduced to the surface models in the direction perpendicular to the surface, which is large enough to avoid interactions between periodic slabs. There were twenty different slab terminations possible for the (100) surface, ten for the (110) surface, and four for the (111) surface. For the surface models, the Brillouin zone integration was carried out using a $2 \times 2 \times 1$ k-point grid centered at the Gamma point. All the structure with different terminations was then allowed to relax unconstrained. The relative stabilities of the Ni-20Cr surfaces were determined according to their relaxed surface energy (γ_r) as given by Eq. (10)⁷⁷:

$$\gamma_r = \frac{1}{2A} (E_{slab}^{relaxed} - NE_{bulk}) \quad (10)$$

Where $E_{slab}^{relaxed}$ is the energy of the slab after relaxation, NE_{bulk} is the energy of an equal number (N) of the bulk Ni-20Cr atoms, A is the slab surface unit area, and the factor of 2 reflects that there are two surfaces for each slab.

Data availability

The digital data for all figures, tables, charts, and any other media contained in this publication and its associated ESI files will be made accessible in the MSEE Community of the Zenodo repository, under Digital Object Identifier (DOI): (TBD).

Received: 19 February 2026; Accepted: 20 August 2026;

Published online: 15 September 2026

References

- Ding, W. & Bauer, T. Progress in research and development of molten chloride salt technology for next generation concentrated solar power plants. *Engineering* **7**, 334–347 (2021).
- LeBlanc, D. Molten salt reactors: a new beginning for an old idea. *Nucl. Eng. Des.* **240**, 1644–1656 (2010).
- Serp, J. et al. The molten salt reactor (MSR) in generation IV: overview and perspectives. *Prog. Nucl. Energy* **77**, 308–319 (2014).
- Goff, M. Non-aqueous processes. *Presentation at "Introduction to Nuclear Fuel Cycle Chemistry"* (2009).
- Marcus, Y. in *Advances in Molten Salt Chemistry: Volume 1* (eds Braunstein, J., Mamantov, G., & Smith, G. P.) 63–127 (Springer US, 1971).
- Parshall, G. W. Catalysis in molten salt media. *J. Am. Chem. Soc.* **94**, 8716–8719 (1972).
- Swinkels, D. A. J. in *Advances in Molten Salt Chemistry: Volume 1* (eds Braunstein, J., Mamantov, G., & Smith, G. P.) 165–223 (Springer US, 1971).
- Beneš, O. & Konings, R. J. M. Thermodynamic evaluation of the NaCl–MgCl₂–UCl₃–PuCl₃ system. *J. Nucl. Mater.* **375**, 202–208 (2008).
- Holcomb, D. E. et al. Fast spectrum molten salt reactor options. *ORNL/TM-2011/105* (2011).
- Sridharan, K. & Allen, T. R. in *Molten Salts Chemistry* (eds Lantelme, F. & Groult, H.) 241–267 (Elsevier, 2013).
- Guo, S., Zhang, J., Wu, W. & Zhou, W. Corrosion in the molten fluoride and chloride salts and materials development for nuclear applications. *Prog. Mater. Sci.* **97**, 448–487 (2018).
- Raiman, S. S. & Lee, S. Aggregation and data analysis of corrosion studies in molten chloride and fluoride salts. *J. Nucl. Mater.* **511**, 523–535 (2018).
- Edeleanu, C. & Littlewood, R. Thermodynamics of corrosion in fused chlorides. *Electrochim. Acta* **3**, 195–207 (1960).
- Sabharwal, P. et al. Advanced heat exchanger development for molten salts. *Nucl. Eng. Des.* **280**, 42–56 (2014).
- McAlpine, S. W., Skowronski, N. C., Zhou, W., Zheng, G. & Short, M. P. Corrosion of commercial alloys in FLiNaK molten salt containing EuF₃ and simulant fission product additives. *J. Nucl. Mater.* **532**, 151994 (2020).
- Liu, X. et al. Temperature-dependent morphological evolution during corrosion of the Ni-20Cr alloy in molten salt revealed by multiscale imaging. *ACS Appl. Mater. Interfaces* **15**, 13772–13782 (2023).
- Zhu, Z. et al. Synergistic effect of irradiation and molten salt corrosion: Acceleration or deceleration? *Corros. Sci.* **185**, 109434 (2021).
- Zhou, W. et al. Proton irradiation-decelerated intergranular corrosion of Ni–Cr alloys in molten salt. *Nat. Commun.* **11**, 3430 (2020).
- Gu, Y., Zhang, W., Xu, Y., Shi, Y. & Volodymyr, K. Stress-assisted corrosion behaviour of Hastelloy N in FLiNaK molten salt environment. *npj Mater. Degrad.* **6**, 90 (2022).
- Zhang, J. Impurities in primary coolant salt of FHRs: chemistry, impact, and removal methods. *Energy Technol* **7**, 1900016 (2019).
- Liu, X. et al. Elucidating the transition of 3D morphological evolution of binary alloys in molten salts with metal ion additives. *ACS Appl. Mater. Interfaces* **16**, 45606–45618 (2024).
- Pavlik, V., Kontrík, M. & Boča, M. Corrosion behavior of Incoloy 800H/HT in the fluoride molten salt FLiNaK + MF_x (MF_x = CrF₃, FeF₂, FeF₃ and NiF₂). *New J. Chem.* **39**, 9841–9847 (2015).
- Bawane, K. et al. Determining oxidation states of transition metals in molten salt corrosion using electron energy loss spectroscopy. *Scripta Materialia* **197**, 113790. <https://doi.org/10.1016/j.scriptamat.2021.113790> (2021).
- Lu, P., Liu, Q., Bao, H., Pan, T. J. & Tang, Z. Effect of FeCl₃ in NaCl–MgCl₂ molten salts on the corrosion behavior of 316 stainless steel at 600 °C. *Corros. Sci.* **212**, 110961 (2023).
- Chang, S., Jia, Y., Du, X. & Guo, S. Corrosion behavior of commercial alloys in LiCl–KCl molten salt containing EuCl₃. *Front. Mater.* **9**, 958296 (2022).
- Li, N., Wang, H., Yin, H., Liu, Q. & Tang, Z. Effect of temperature and impurity content to control corrosion of 316 stainless steel in molten KCl–MgCl₂ salt. *Materials* **16**, 2025 (2023).
- Ding, W., Gomez-Vidal, J., Bonk, A. & Bauer, T. Molten chloride salts for next generation CSP plants: electrolytical salt purification for reducing corrosive impurity level. *Sol. Energy. Mat. Sol. C.* **199**, 8–15 (2019).
- Kruizenga, A. M. Corrosion mechanisms in chloride and carbonate salts. (Sandia National Laboratories (SNL), 2012).
- Bawane, K. et al. Visualizing time-dependent microstructural and chemical evolution during molten salt corrosion of Ni-20Cr model alloy using correlative quasi in situ TEM and in situ synchrotron X-ray nano-tomography. *Corros. Sci.* **195**, 109962 (2022).
- Yang, Y. et al. One dimensional wormhole corrosion in metals. *Nat. Commun.* **14**, 988 (2023).
- Liu, X. et al. Formation of three-dimensional bicontinuous structures via molten salt dealloying studied in real-time by in situ synchrotron X-ray nano-tomography. *Nat. Commun.* **12**, 3441 (2021).
- Guo, S., Zhuo, W., Wang, Y. & Zhang, J. Europium induced alloy corrosion and cracking in molten chloride media for nuclear applications. *Corros. Sci.* **163**, 108279 (2020).
- Zhang, J. Electrochemistry of actinides and fission products in molten salts—Data review. *J. Nucl. Mater.* **447**, 271–284 (2014).

34. Laitinen, H. A. & Liu, C. H. An electromotive force series in molten lithium chloride-potassium chloride eutectic. *J. Am. Chem. Soc.* **80**, 1015–1020 (1958).
35. Peng, Y. et al. Unraveling impurity-dependent morphological and chemical evolution of Ni–20Cr alloy in eutectic LiCl–KCl molten salt. *ACS Appl. Mater. Interfaces* (2025).
36. Chan, H. L. et al. Morphological evolution and dealloying during corrosion of Ni20Cr (wt.%) in molten FLiNaK salts. *J. Electrochem. Soc.* **171**, 081501 (2024).
37. Chan, H. L. et al. Corrosion electrochemistry of chromium in molten FLiNaK salt at 600. *C. J. Electrochem. Soc.* **170**, 081502 (2023).
38. Roine, A. *HSC Chemistry [Software]*, Metso, Pori. Software available at. www.metso.com/hsc, (2023).
39. Chang, S., Jia, Y., Du, X. & Guo, S. Corrosion behavior of commercial alloys in LiCl–KCl molten salt containing EuCl₃. *Frontiers in Materials* **9**, 958296 (2022).
40. De Córdoba, G. & Caravaca, C. Potentiometric study of Sm–O compounds formation in the molten LiCl–KCl eutectic at 450°C. Determination of a E–pO₂– stability diagram. *J. Phys. Chem. Solids* **67**, 1862–1868 (2006).
41. Feng, X. K. & Melendres, C. A. Anodic corrosion and passivation behavior of some metals in molten LiCl–KCl containing oxide ions. *J. Electrochem. Soc.* **129**, 1245 (1982).
42. Horvath, D. & Simpson, M. F. Electrochemical monitoring of Ni corrosion induced by water in eutectic LiCl–KCl. *J. Electrochem. Soc.* **165**, C226 (2018).
43. Guo, L., Yue, Y., Pan, T. J., Tang, Z. F. & Liu, W. Corrosion behavior of Ni–Al alloys beneath chlorides melt salt at 700 °C. *Sol. Energy* **184**, 657–663 (2019).
44. Ishitsuka, T. & Nose, K. Solubility study on protective oxide films in molten chlorides created by refuse incineration environment. *Mater. Corros.* **51**, 177–181 (2000).
45. Wang, C., Chen, W., Chen, M., Chen, D. & Yang, K. Corrosion behavior and elements interdiffusion between a Ni coating and GH3535 alloy with and without a CrN barrier in molten fluoride salts. *J. Nucl. Mater.* **514**, 348–357 (2019).
46. Olson, L., Sridharan, K., Anderson, M. & Allen, T. Nickel-plating for active metal dissolution resistance in molten fluoride salts. *J. Nucl. Mater.* **411**, 51–59 (2011).
47. Bhavé, C. & Tonks, M. R. The effect of nickel coatings on corrosion of nickel-chrome alloys in molten FLiBe determined using a phase-field model. *J. Nucl. Mater.* **606**, 155616 (2025).
48. Kondaiah, P. & Pitchumani, R. Electrodeposited nickel coatings for exceptional corrosion mitigation in industrial grade molten chloride salts for concentrating solar power. *Renew. Sust. Energ. Rev.* **189**, 113848 (2024).
49. Weinstein, M. et al. Environmental degradation of electroplated nickel and copper coated SS316H in molten FLiNaK salt. *Corros. Sci.* **191**, 109735 (2021).
50. Zhu, H., Li, B., Chen, M., Qiu, C. & Tang, Z. Improvement of corrosion resistance of Hastelloy–N alloy in LiF–NaF–KF molten salt by laser cladding pure metallic coatings. *Coatings* **8**, 322 (2018).
51. Ronne, A. et al. Revealing 3D morphological and chemical evolution mechanisms of metals in molten salt by multimodal microscopy. *ACS Appl. Mater. Interfaces* **12**, 17321–17333 (2020).
52. Gill, S. K. et al. Investigating corrosion behavior of Ni and Ni–20Cr in molten ZnCl₂. *Corros. Sci.* **179**, 109105 (2021).
53. Chan, H. L., Romanovskaia, E., Qiu, J., Hosemann, P. & Scully, J. R. Insights on the corrosion thermodynamics of chromium in molten LiF–NaF–KF eutectic salts. *npj Mater. Degrad.* **6**, 46 (2022).
54. Mills, S. H. et al. Elucidating the role of Cr migration in Ni–Cr exposed to molten FLiNaK via multiscale characterization. *Acta Mater* **279**, 120206 (2024).
55. Moulin, P., Huntz, A. M. & Lacombe, P. Influence du carbone sur la diffusion du chrome et du nickel en volume et dans les joints de grains de l’alliage Ni–Cr 80/20. *Acta Metall* **27**, 1431–1443 (1979).
56. Chen, T.-F., Tiwari, G. P., Iijima, Y. & Yamauchi, K. Volume and grain boundary diffusion of chromium in Ni–base Ni–Cr–Fe alloys. *Mater. Trans.* **44**, 40–46 (2003).
57. Seybolt, A. U. Oxidation of Ni–20 Cr alloy and stainless steels in the presence of chlorides. *Oxid. Met.* **2**, 119–143 (1970).
58. Evered, C. et al. Synergistic effects of irradiation and molten salt corrosion influenced by grain boundary types and crystallographic orientation. *Corros. Sci.* **258**, 113385 (2026).
59. Zhu, L. & Li, Y. Cleavage-dissolution assisted stress corrosion cracking under elastic loads. *npj Mater. Degrad.* **5**, 25 (2021).
60. Aagesen, L. K., Coltrin, M. E., Han, J. & Thornton, K. Phase-field simulations of GaN growth by selective area epitaxy from complex mask geometries. *J. Appl. Phys.* **117**, 194302 (2015).
61. Sahu, S. & Frankel, G. S. Phase field modeling of crystallographic corrosion pits. *J. Electrochem. Soc.* **169**, 020557 (2022).
62. Arkoub, H., Dwivedi, S., van Duin, A. C. T. & Jin, M. A reactive force field approach to modeling corrosion of NiCr alloys in molten FLiNaK salts. *Appl. Sur. Sci.* **655**, 159627 (2024).
63. Sun, X.-F., Wang, H.-T. & Han, E.-H. Effect of Cr doping on the surface characteristics of Ni metal studied with first-principles calculation. *Acta Metall. Sin.* **32**, 461–470 (2019).
64. Arkoub, H., Flynn, D., van Duin, A. C. T. & Jin, M. Surface orientation-dependent corrosion behavior of NiCr alloys in molten FLiNaK salt. *ACS Appl. Mater. Interfaces* **17**, 38708–38719 (2025).
65. Phillips, W. C. et al. Design and performance of high-temperature furnace and cell holder for in situ spectroscopic, electrochemical, and radiolytic investigations of molten salts. *Rev. Sci. Instrum.* **91**, 083105 (2020).
66. Arganda-Carreras, I. et al. Trainable Weka Segmentation: a machine learning tool for microscopy pixel classification. *Bioinformatics* **33**, 2424–2426 (2017).
67. Hovden, R. et al. Repeatable and transferable processing for electron tomography: an open platform for visualization and reconstruction of 3D materials. *Microsc. Microanal.* **21**, 2407–2408 (2015).
68. Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* **136**, B864–B871 (1964).
69. Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**, A1133–A1138 (1965).
70. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
71. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
72. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
73. Zunger, A., Wei, S. H., Ferreira, L. G. & Bernard, J. E. Special quasirandom structures. *Phys. Rev. Lett.* **65**, 353–356 (1990).
74. van de Walle, A., Asta, M. & Ceder, G. The alloy theoretic automated toolkit: a user guide. *Calphad* **26**, 539–553 (2002).
75. Methfessel, M. & Paxton, A. T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* **40**, 3616–3621 (1989).
76. Ong, S. P. et al. Python materials genomics (pymatgen): a robust, open-source python library for materials analysis. *Comput. Mater. Sci.* **68**, 314–319 (2013).
77. Xiao, H. et al. Effects of Zr doping on the surface energy and surface structure of UO₂: atomistic simulations. *Appl. Sur. Sci.* **351**, 517–523 (2015).

Acknowledgements

This work was supported as part of the Molten Salts (MSEE) in Extreme Environments Energy Frontier Research Center, funded by the US

Department of Energy (DOE), Office of Science. Brookhaven National Laboratory and Idaho National Laboratory are operated under DOE contracts DE-SC0012704 and DE-AC07-05ID14517, respectively. Work at Stony Brook University and the University of Michigan was supported by MSEE through subcontracts from BNL. The authors also acknowledge the U.S. Department of Energy, Office of Nuclear Energy, under DOE Idaho Operations Office Contract DE-AC07-05ID14517, for use of the resources as part of Nuclear Science User Facilities. The authors thank Jana Howard, Ching-Heng Shiao, Yaqiao Wu at Center for Advanced Energy Studies and Jayson Bush and Jeremy Burgener at Idaho National Laboratory for their invaluable assistance. The authors thank Dr. Jian Gan and Dr. Chaitanya Bhave from INL for valuable discussions on the results.

Author contributions

Kaustubh Bawane: Conceptualization, Investigation, Methodology, Writing – original draft preparation. Yuxiang Peng: Investigation, Methodology, Writing – original draft preparation, Writing – review and editing. Linu Malakkal: Investigation, Methodology, Writing – original draft preparation. Writing – review and editing. Mario Matos: Investigation, Methodology. William Phillips: Investigation, Methodology. Katsuyo Thornton: Supervision, Funding acquisition, Writing – review and editing. James F. Wishart: Supervision, Funding acquisition, Project administration, Writing – review and editing. Yu-chen Karen Chen-Wiegar: Supervision, Funding acquisition, Writing – review and editing. Ruchi Gakhar: Conceptualization, Supervision, Funding acquisition, Investigation, Methodology, Writing – review and editing.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41529-026-00874-w>.

Correspondence and requests for materials should be addressed to Kaustubh Bawane or Ruchi Gakhar.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2026

This Article in Press is shared early to give you faster access to new research. It is citable and carries a permanent DOI. The final edited version will replace it automatically.