

Corrosion of alloys in a chloride molten salt (NaCl-LiCl) for solar thermal technologies



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ABSTRACT

Next-generation solar power conversion systems in concentrating solar power (CSP) applications require high-temperature advanced fluids in the range of 600–800 °C. Current commercial CSP plants use molten nitrate salt mixtures as the heat transfer fluid and the thermal energy storage (TES) media while operating with multiple hours of energy capacity and at temperatures lower than 565 °C. At higher temperatures, the nitrates cannot be used because they decompose. Molten chloride salts are candidates for CSP applications because of their high decomposition temperatures and good thermal properties; but they can be corrosive to common alloys used in vessels, heat exchangers, and piping at these elevated temperatures. In this article, we present the results of the corrosion evaluations of several alloys in eutectic 34.42 wt% NaCl – 65.58 wt% LiCl at 650–700 °C in nitrogen atmosphere. Electrochemical evaluations were performed using open-circuit potential followed by a potentiodynamic polarization sweep. Corrosion rates were determined using Tafel slopes and Faraday's law. A temperature increase of as little as 50 °C more than doubled the corrosion rate of AISI stainless steel 310 and Incoloy 800H compared to the initial 650 °C test. These alloys exhibited localized corrosion. Inconel 625 was the most corrosion-resistant alloy with a corrosion rate of 2.80 ± 0.38 mm/year. For TES applications, corrosion rates with magnitudes of a few millimeters per year are not acceptable because of economic considerations. Additionally, localized corrosion (intergranular or pitting) can be catastrophic. Thus, corrosion-mitigation approaches are required for advanced CSP plants to be commercially viable.

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1. Introduction

Thermal energy storage (TES) is a key component of concentrating solar power (CSP) plants and grid integration of renewable energies as a whole. Although energy may be stored by several different methods such as pumped hydro, batteries, or supercapacitors, TES has the advantages of lower capital costs and high operating efficiencies [1]. The most obvious benefit of TES is that it allows for power generation not only during peak solar irradiance, but also, during peak demand that occurs later in the day. TES also stabilizes energy generation from fluctuations such as cloud cover. This makes concentrating solar power with thermal energy storage (CSP/TES) a dispatchable resource. In addition, the nature of the CSP/TES power plant allows for fast ramp rates. The flexibility inherent to solar fields with TES allows greater penetration of other non-dispatchable renewable resources such as solar photovoltaics (PV) [2]. As PV penetration increases, increased strain is placed on conventional systems to rapidly ramp power

generation to compensate for the reduced solar output at the end of the day. In addition to the problem of the ramp rate, conventional systems are limited in the overall ramp range. The dispatchable power provided by CSP/TES fields can accommodate these demands, thus allowing for greater PV use in addition to the benefits of the CSP plants themselves.

Molten-salt TES may be used in several configurations in a CSP field. In active storage systems, the storage media is actively circulated for heating; in passive storage systems, the heat transfer fluid (HTF) flows through the storage for charging and discharging [3]. Active systems are further classified into direct and indirect systems. In direct active systems, the HTF is also the storage media and is heated directly from the source. For indirect active systems, the HTF is heated in the field, and thermal energy is transferred to the storage media through a heat exchanger. Active systems will either employ a two-tank system, where the hot and cold storage media are separated, or a single-tank system, where the hot and cold fluids are stored together. The hot and cold fluids remain separated by buoyancy effects, with a thermocline region established between the fluids at different temperatures [1]. Thermocline systems typically require a filler material to help maintain the temperature gradient. Generally, the two-tank system is more

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widely implemented, but advances by Sandia National Laboratories are promising for single-tank systems. Currently, seven parabolic trough systems use a two-tank indirect configuration, one trough system uses a two-tank direct system, and a central receiver with a two-tank direct configuration is operating that implements a TES application with molten salts [1]. The nominal maximum operating temperatures for those plants are 386°, 550°, and 565 °C, respectively.

Molten salts can be used as HTF and TES as sensible or latent-heat media. Current CSP plants use nitrate molten salts and can operate with multiple hours of energy storage capacity. Next-generation solar power conversion systems in CSP applications are targeting high-temperature, advanced fluids to operate in the range of 600–800 °C, which are temperatures that exceed the range of nitrate stability. Chloride molten salts are promising candidates, but are corrosive to common alloys used in vessels, heat exchangers, and piping at these elevated temperatures [4]. Containment material degradation is a major concern to meet commercial viability of next generation CSP plants [5]. The chemical interactions between these fluids and the metallic containments must be evaluated and understood to determine the degradation and lifetime of the containment material. Therefore, we must establish corrosion performance limits under various conditions and material systems to select the most cost-effective materials for these plants. The chemical (or electrochemical) reactions and transport modes are complex for molten salt corrosion in systems involving multi-component alloys and salts; but some insight can be gained through thermochemical models to identify major reactions [6]. Electrochemical techniques for molten salt corrosion can be used to rapidly identify the best-performing alloys. Recently, these techniques have been used for a better understanding of the fundamentals behind the molten salt corrosion mechanisms for thin-film molten salts in gas-turbine engines and electric power generation [7–10]. Molten-salt corrosion of Inconel 625 (IN625) in salts containing sulfates, oxides, and chlorides at 600°, 700°, and 800 °C reported corrosion rates of 1.80 ± 0.33 , 14.25 ± 2.01 , and 26.54 ± 1.69 mm/year, respectively. IN625 was not able to passivate under the conditions tested; specifically, the oxide scale produced was not protective against the corrosive salt [11].

It has been reported that Cr is not an effective element for improving corrosion resistance of Fe-based and Ni-based alloys. Because Cr_2O_3 has a higher solubility than iron and nickel oxides, it will react more readily with chloride salt [12,13]. This high solubility is reported for KCl-containing molten salts in oxidizing atmospheres, in which soluble K-chromates are formed. The higher the Ni content, the higher the corrosion resistance against molten chlorides [7]. Intergranular corrosion is the major corrosion type found in alloys exposed to molten chlorides in oxidizing atmospheres [6].

Potentiodynamic polarization sweep (PPS) is a powerful electrochemical technique that has been used to measure molten salt corrosion of stainless steels (SS) because it generates data quickly and is sensitive to very low corrosion rates [7]. Before the PPS, the open-circuit potential (OCP) must be established. The OCP is the stable electric potential obtained between the metal surface and the electrolyte (molten salt). To initiate the PPS, the metal/electrolyte system is first cathodically polarized (negative overpotential from the OCP), followed by a sweep in applied potential toward anodic polarization (positive overpotential from OCP). The polarization curves (applied potential vs measured current density) are then used to find the cathodic and anodic Tafel slopes. These slopes are usually found between ± 30 – 120 mV relative to the sample-OCP [14]. The intersection of the Tafel slopes provides the corrosion potential (E_{corr}) and corrosion current density (j_{corr}), which is the corrosion current (i_{corr}) divided by the exposed area

(A).

The corrosion rate (CR) in millimeters per year can be calculated using the Stern-Gear equation through Faraday's law [15,16]:

$$CR = \frac{j_{corr} \cdot K \cdot EW}{\rho}, \quad (1)$$

where K is a constant equal to 3272 [mm/(A cm year)], EW is the equivalent weight of the alloy [g/mole-e⁻], and ρ is the alloy density [g/cm³].

The equivalent weight of the alloy is calculated using its composition and the following equations:

$$EW = NEQ^{-1} \quad (2)$$

$$NEQ = \sum \left(\frac{f_i \cdot n_i}{MW_i} \right) \quad (3)$$

where NEQ is the number of equivalent; f_i is the weight fraction; n_i is the number of electrons being transferred, and MW_i is the atomic weight.

In addition to identifying corrosion currents and potentials, the polarization curves may also be used to determine the corrosion behavior of the sample. If the current constantly increases with the applied potential, then the sample has active corrosion. If the current decreases to values lower than i_{corr} and remains at that value for a certain potential range, then the sample is showing passivation produced by the formation of protective scales at the surface.

Using these techniques, scientists at the National Renewable Energy Laboratory (NREL) evaluated several alloys in eutectic 34.42 wt% NaCl – 65.58 wt% LiCl at 650° and 700 °C in a nitrogen atmosphere.

2. Experiment

2.1. Preparation of salt mixture

The eutectic 34.42 wt% NaCl – 65.58 wt% LiCl with a melting point of 554 °C was selected because it has a high heat capacity of 1.44 J/g. K. The eutectic salt mixture was prepared using ACS grade anhydrous NaCl and LiCl, each with a purity greater than 99 wt%, as received from Alfa Aesar. The unmixed salts were placed in a drying oven (DK-42, American Scientific Products) at 120 °C in air for at least 24 h to ensure low moisture content. The salts were weighed and mixed to the proper ratio in 125-g batches. The salts were then placed in an alumina crucible because this material has been shown to be stable in chloride molten-salt systems. The crucible containing the salt mixture was kept in a vacuum furnace at 120 °C for 24 h and then transferred to a muffle furnace (Vulcan 3-1750), heated and held at 300 °C for three hours. The temperature was then raised to 850 °C, where it was maintained for 30 min to completely melt the components. To avoid moisture absorption after cooling, the pre-melted and solidified salt mixture was stored at 120 °C in the vacuum furnace until needed for testing. Since the CSP plants cannot pursue very complicated and expensive mixing and melting procedures of the salts, the salt preparation followed here did not consider any further purification of the mixture.

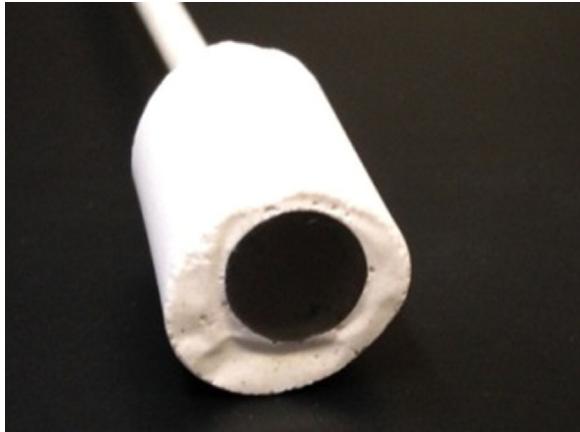
2.2. Preparation of alloys

The alloys tested were SS347, SS310, Incoloy (In) 800H, and Inconel (IN) 625. The nominal composition of the alloys is shown in Table 1. Cylinders of 8-mm diameter and 12-mm height were

Table 1.

Nominal composition of the alloys.

Alloy	Composition [wt%]												
	Fe	Cr	Ni	Mn	Al	Mo	Si	C	Cu	Ti	Co	Ta	Nb
SS310	50.75	25	20.5	2			1.5	0.25					
SS347	68.53	17.67	9.62	1.66		0.38	0.77	0.051	0.38		0.2	0.021	0.72
In800H	44.89	19.63	33.17	0.77	0.46		0.29	0.06	0.2	0.53			
IN625	5	21.5	58			9						3.55	

**Fig. 1.** Encapsulated sample (working electrode) for corrosion testing.

machined from each alloy. They were progressively polished using up to a 1200-grit SiC abrasive paper, cleaned with deionized water, and dried with acetone and compressed air. Electrical connection of each sample, or working electrode (WE), was obtained using nickel-chromium wire (0.5-mm diameter) tightly tied around a 1.5-mm groove at the top section of each cylinder. To control the amount of metallic area exposed to the molten salt, the samples

were encapsulated using silicon-dioxide-based ceramic cement (Aremco 645-N) with a boron nitride thin film on the surface, as shown in Fig. 1. The boron nitride was applied by spraying a BN aerosol from ZYP Coatings, Inc on top of cured Aremco 645-N cement. This configuration has shown to avoid salt penetration towards the encapsulated metal surface [17]. The curing procedure used was recommended by the vendors.

2.3. Electrochemical corrosion tests

To electrochemically study the alloy's corrosion behavior, we employed a three-electrode arrangement. The pseudo-reference electrode (RE) was made with Pt wire (0.5-mm diameter) and the working electrode (WE) as the sample of interest. The counter electrode (CE) was made from a 2.5 cm × 2.5 cm Pt-gauze (100 mesh) folded to a 1 cm × 1 cm and spot welded to a 0.5-mm diameter Pt-wire. The pre-melted chloride mixture and the three-electrode arrangement were placed inside a high-temperature electrochemical cell. Fig. 2 shows the schematic of the electrochemical cell (2a) and the three-electrode arrangement (2b). To perform the OCP and PPS, the potential and current of the WE with respect to the Pt-wire pseudo-RE was measured with a potentiostat (AUTOLAB-PGSTAT302N). The Pt and Ni-Cr wires were electrically insulated in 1/8" alumina tubes, and silica-based refractory cement was used to seal the tubes.

The temperature near the electrodes was recorded during

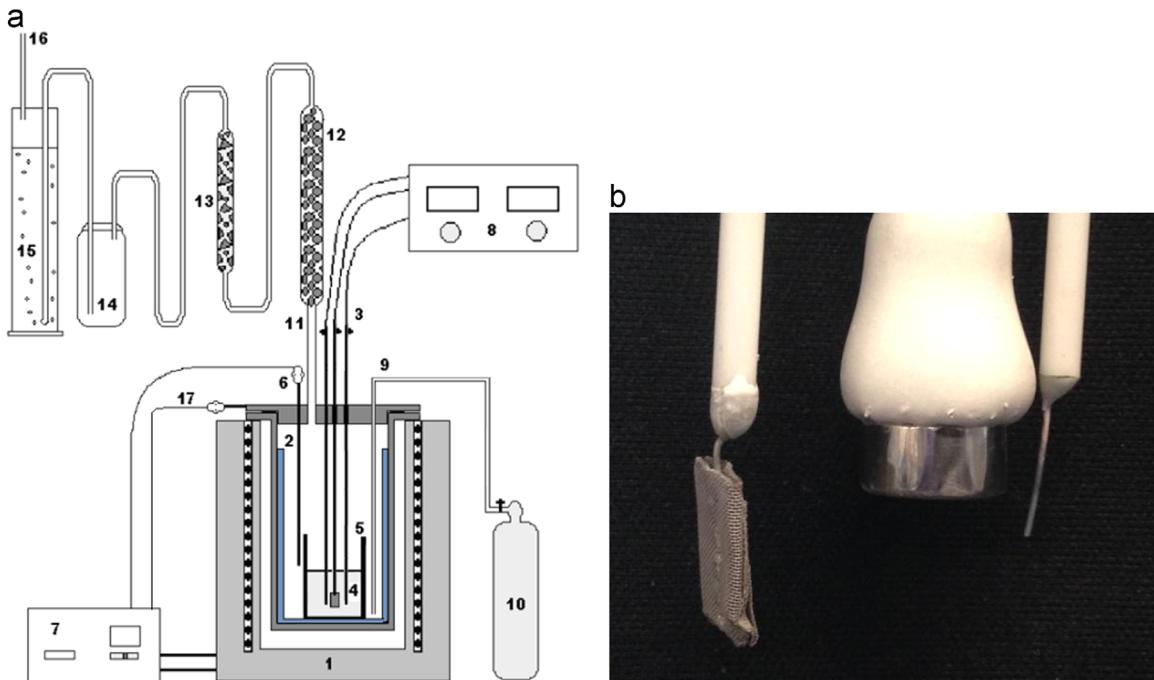


Fig. 2. (a) schematic of the high-temperature electrochemical cell and off-gas system: 1: crucible furnace; 2: quartz liner; 3: three-electrode arrangement (RE: reference electrode, CE: counter electrode; WE: working electrode or sample); 4: molten salt; 5: alumina crucible; 6: thermocouple; 7: furnace controller; 8: potentiostat; 9: gas inlet; 10: carrier gas; 11: off-gas system (which consists of 12: MgO trap for chlorine; 13: moisture removal; 14: water reflux; 15: 1 M NaOH scrubber; and 16: gas exhaust); and 17: lid thermocouple and (b) three-electrode arrangement (left to right: CE, WE, and RE).

corrosion testing with a Type K thermocouple. The electrochemical cell was sealed and purged with nitrogen. The off-gas passed through a series of traps to remove hazardous chlorine vapors before being vented to local exhaust. The off-gas treatment consisted of MgO pellets, moisture removal using anhydrous CaSO_4 , a reflux trap, and a 1 M NaOH scrubber.

The required stabilization time of the Pt-RE in molten 34.42 wt% NaCl – 65.58 wt% LiCl was determined. For this purpose, we monitored the change in the undisturbed potential (E) as a function of time (t) until it showed stabilization. This same period of time was used in future tests to allow the RE and CE to come to equilibrium before immersing the WE.

For the corrosion tests, a crucible furnace (Lindberg CF56822C) containing the electrochemical cell, with the salt and electrodes, was slowly heated to the testing temperature to avoid the fracture of the fully cured cement used to encapsulate and seal the electrodes. Once at temperature the system was allowed to stabilize for one hour, then the RE and CE were immersed and allowed to reach potential equilibration. Once the encapsulated alloy was immersed, its potential vs. the pseudo Pt-RE was recorded. The alloy's OCP was established when the potential reached quasi-equilibrium ($dE/dt \leq 100 \mu\text{V/s}$). Once the WE-OCP was identified, the PPS test was performed by applying cathodic (–) and anodic (+) external potentials, sweeping from –0.35 V to +0.6 V relative to the OCP value in 0.001 V steps at 0.001 V/s. More than five coupons of each alloy were tested under the same conditions to evaluate the reproducibility of the results. Some results were discarded based on the behavior of the PPS curves.

2.4. Characterization of alloys and salts

The alloys were metallographically characterized before and after the corrosion tests using a field-emission scanning electron microscope (FESEM). Chemical analysis of the samples was performed using energy-dispersive X-ray spectrometry (EDX). Top-view micrographs of the corroded samples were taken at different magnification.

The corroded and dissolved elements from the alloys into the molten salts were determined from salt samples after corrosion using inductively coupled plasma-mass spectroscopy (ICP-MS). To determine the chemical composition baseline of the salt matrix, samples for the original salt composition (34.42 wt% NaCl – 65.58 wt% LiCl) were analyzed before degradation testing. Additionally, three degradation tests of just the cured cement immersed in the molten salt were performed at the same corrosion conditions used for the alloys; the salt samples were analyzed using ICP-MS. Chemical composition of the salt after corrosion was corrected by subtracting the baseline and the cement's dissolved element, which allowed for analysis of corrosion products while accounting for the test conditions.

3. Results and discussion

3.1. Corrosion tests

The electrical stabilization of the pseudo-RE vs. CE in the molten eutectic 34.42 wt% NaCl – 65.58 wt% LiCl is shown in Fig. 3. To start the corrosion test, the RE and CE were immersed into the molten salt and allowed to stabilize for at least 45 min. Then the WE was immersed and the voltage was recorded as a function of time to determine the equilibration point in which the OCP is stabilized. After this, cathodic and anodic overpotentials were applied and PPS curves were obtained. Typical polarization curves (applied potential vs log of current density) of the alloys are shown in Figs. 4 and 5.

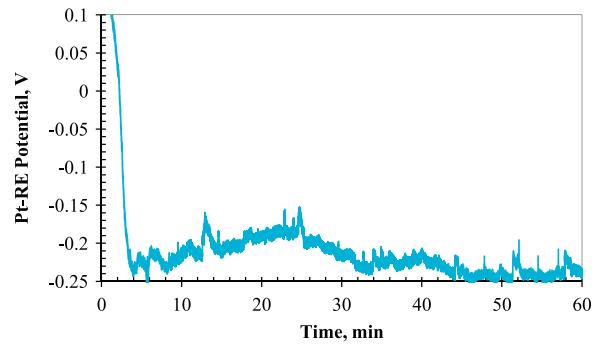


Fig. 3. Potential stabilization of the Pt-RE vs. Pt-CE in the molten eutectic 34.42 wt% NaCl – 65.58 wt% LiCl at 650 °C under nitrogen.

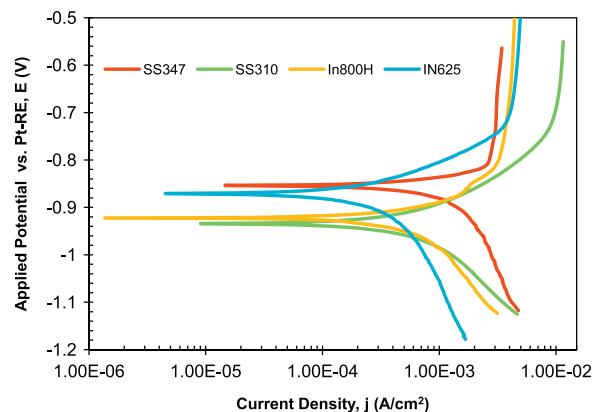


Fig. 4. Polarization curves of alloys in 34.42 wt% NaCl – 65.58 wt% LiCl at 650 °C under nitrogen.

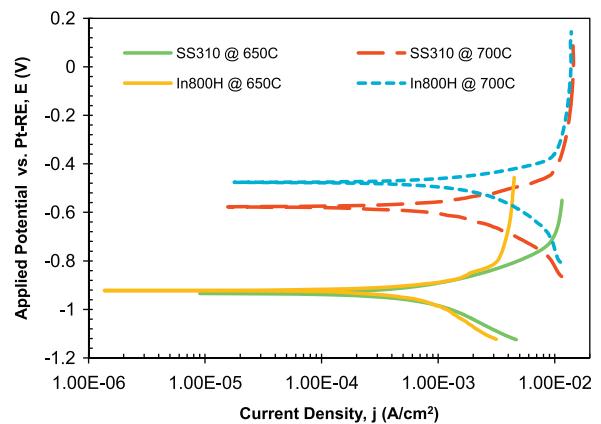


Fig. 5. Polarization curves of SS310 and In800H in 34.42 wt% NaCl – 65.58 wt% LiCl at 650° and 700 °C under nitrogen.

Fig. 4 shows the polarization curves of the tested alloys at 650 °C. The alloys appear to be exhibiting active corrosion. This means that the specimen is degrading across all applied anodic overpotentials. At higher anodic overpotentials, the current density stabilized, showing diffusion control. This behavior is expected because the corrosion is limited by diffusion of ionic species away from the metallic surface. Fig. 5 shows the increase in corrosion current density—and thus, corrosion rates—of SS310 and In800H when temperature is increased from 650° to 700 °C.

The polarization curves were used to determine the intersection of the Tafel slopes, which yields the E_{corr} and the j_{corr} . Using Eq. (1) and the alloys characteristics from Table 2, we calculated the corrosion rates of each alloy. Table 3 shows the corrosion results of the alloys at 650 °C. Corrosion at 700 °C was also

Table 2.

Density (ρ) and equivalent weight (EW) of the alloys.

Alloy	ρ [g/cm ³]	EW [g/mole-e ⁻]
SS347	7.96	25.57
SS310	7.89	24.75
In800H	7.94	25.04
IN625	8.44	24.63

Table 3.

Corrosion data (average \pm 1 standard deviation) of tested alloys in 34.42 wt% NaCl – 65.58 wt% LiCl.

Alloy	OCP vs. pseu-do-RE [mV]	E _{corr} vs. pseu-do-RE [mV]	j _{corr} [μA/cm ²]	CR [mm/year]
650 °C				
SS347	-784 ± 113	-847 ± 91	713.00 ± 30.74	7.49 ± 0.32
SS310	-888 ± 170	-938 ± 218	626.16 ± 38.72	6.42 ± 0.40
In800H	-876 ± 32	-910 ± 22	573.79 ± 34.19	5.94 ± 0.33
IN625	-849 ± 73	-856 ± 57	233.00 ± 94.68	2.80 ± 0.38
700 °C				
SS310	-506 ± 70	-571 ± 75	1213.61 ± 148.10	12.45 ± 1.52
In800H	-453 ± 5	-474 ± 3	1387.79 ± 131.96	14.31 ± 1.36

Open-circuit potential (OCP), corrosion potential (E_{corr}), corrosion current density (j_{corr}), and corrosion rate (CR).

performed for alloys SS310 and In800H. The most corroded alloy was SS347, which can be seen in Fig. 4 with the highest current density; it had a corrosion rate of 7.49 ± 0.32 mm/year. High nickel content is required for corrosion-resistance behavior against molten chloride systems, and this alloy has a very low nickel concentration of only 9.62 wt%.

Fig. 4 shows that SS310 and In800H curves are similar. The Tafel slope intercept is very close for these two alloys. Their corrosion rates are quite similar (6.42 ± 0.40 mm/year for SS310 and 5.94 ± 0.33 mm/year for In800H). In800H has a lower chromium content (19.63 wt% Cr) than SS310 (25 wt% Cr) and a higher nickel content (33.17 wt% Ni vs. ~20.5 wt% Ni in SS310). We cannot explain which element contributes the most to the corrosion mechanisms of the alloy, and further studies are required, such as electrochemical impedance spectroscopy and long-term weight loss/gain corrosion tests.

The alloy with the highest corrosion resistance against molten NaCl–LiCl at 650 °C was IN625 with a corrosion rate of 2.80 ± 0.38 mm/year. IN625 is designed to have high corrosion resistance and to maintain its mechanical properties at high temperatures. It is a nickel superalloy (> 58 wt% Ni) with a minimum amount of iron (< 5 wt% Fe). It has been reported that high Ni content in alloys is very effective in improving the corrosion resistance against molten chlorides whereas Cr plays a detrimental role [7]. The corrosion of multicomponent alloys is complex, exhibiting several mechanisms and with different metals corroding in parallel—one of them degrading faster than the others. The recorded corrosion current associated with the calculated corrosion rate is the product of several elements corroding. Further analyses are required to better understand the corrosion mechanisms involved. Since the salts used were not further purified, impurities such as oxides, residual moisture and possible oxidizers may play an important role in corrosion in molten salts. Because of this, extensive chemical analyzes of the selected system (alloy/salts) must be determined to establish the corrosion mechanisms and thus design the corrosion mitigation approaches that could be chemical control of the molten salt or surface treatments of the alloys.

The effect of temperature on the corrosion rates of alloys in

molten 34.42 wt% NaCl – 65.58 wt% LiCl was evaluated with SS310 and In800H. Fig. 5 shows the polarization curves for these alloys at 650 °C (solid lines) and 700 °C (dashed lines). It is clear that corrosion of the alloys increases with temperature. An increase of just 50 °C produced an increase of more than twice the corrosion rates of these alloys. The corrosion rates of SS310 increased from 6.42 ± 0.40 mm/year to 12.45 ± 1.52 mm/year and In800H increased from 5.94 ± 0.33 mm/year to 14.31 ± 1.36 mm/year. Porcayo-Calderon et al. [7] reported corrosion current densities of Ni20Cr in KCl–ZnCl₂ at 450 °C that are one order of magnitude higher than the results obtained at 650 °C in this investigation. These higher corrosion rates are likely due to those evaluations being performed in static air, whereas in this investigation we employed nitrogen atmosphere. The higher the concentration of oxygen dissolved, the higher the oxidation potential of the molten salt—and thus, the higher the degradation. When the cover gas and/or an oxidizer coming from salt impurities can ionically dissociate and dissolved into an electrolyte they can generate secondary cathodic reactions that will participate in the corrosion process. When this occurs more electronic transfer is required and the anode must delivered more electrons and thus more corrosion occurs.

For TES applications, corrosion rates of these magnitudes cannot be sustained. Similar corrosion behavior was obtained by Mohammadi-Zahrani and Alfantazi [11] for IN625 in molten PbSO₄–ZnO–Pb₃O₄–Fe₂O₃–PbCl₂. Corrosion rates at 600°, 700°, and 800 °C were 1.80 ± 0.33 , 14.25 ± 2.01 , and 26.54 ± 1.69 mm/year, respectively. These results show that the use of molten-salts containment materials requires corrosion-mitigation approaches to have effective TES systems. Molten salt chemical control such as oxidizer and moisture elimination by implementing cost-effective purification processes and atmosphere control to avoid oxygen and moisture absorption during operation must be considered.

3.2. Characterization of corroded alloys and salts

The alloys were metallographically characterized with FESEM-EDX before and after corrosion tests. EDX analyses of the alloys before corrosion tests were used to determine the baseline composition and thus compare the surface chemical composition change after degradation. Top-view micrographs of low and high magnification of the corroded SS310, In800H, and IN625 samples are shown in Fig. 6. The surface analysis of these alloys shows that In800H is more corrosion resistant than SS310; but at higher magnification (Fig. 6(b) and (d)), we see that both alloys might have localized corrosion. Many pits may be observed at the surface of these two alloys. It is known that intergranular and pitting corrosion are very common in chloride systems, and the failure of the alloys because of this localized corrosion type can be catastrophic.

Figs. 7–9 show the surface areas and phases analyzed by EDX after corrosion. Comparing the chemical composition of the non-corroded SS310 (Fig. 7(a)) with the regions analyzed after corrosion (Fig. 7(b) to e), the EDX of the corroded surface showed chromium depletion and a lower iron content at the alloy's surface. The analyzed region in Fig. 7(b) shows Cr depletion with low amounts of Fe, very high Ni content, and the presence of O. Fig. 7(c) resolved the area with an oxide enriched in Ni with small amounts of Fe and Cr. The zone analyzed in Fig. 7(d) exhibits the presence of a Fe–Cr oxide. Fig. 7(e) shows a particle identified as Cr oxide. Chromium has been reported to play an important role in the degradation of alloys in chloride systems [12,13]. It has been proposed that Cr and/or Cr₂O₃ are attacked by Cl compounds to form chromium chloride, thus depleting the alloy of this protective element. The proposed mechanism is that CrCl₃ will migrate at the alloy's surface, reoxidize to Cr₂O₃, and form precipitates that are

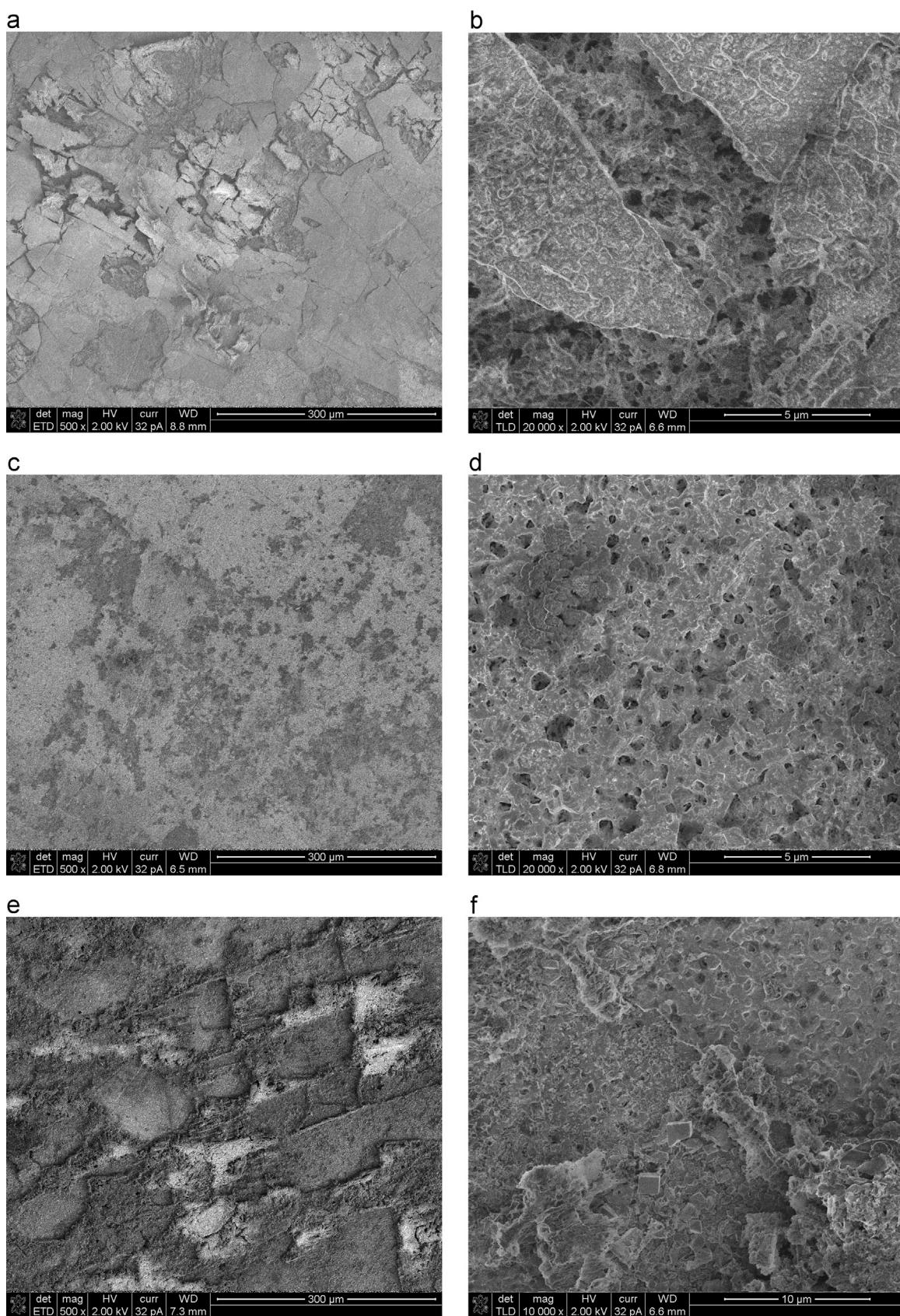


Fig. 6. FESEM top-view micrographs at different magnifications of the corroded alloys in 34.42 wt% NaCl – 65.58 wt% LiCl at 650 °C. SS310 (a) and (b); In800H (c) and (d); and IN625 (e) and (f).

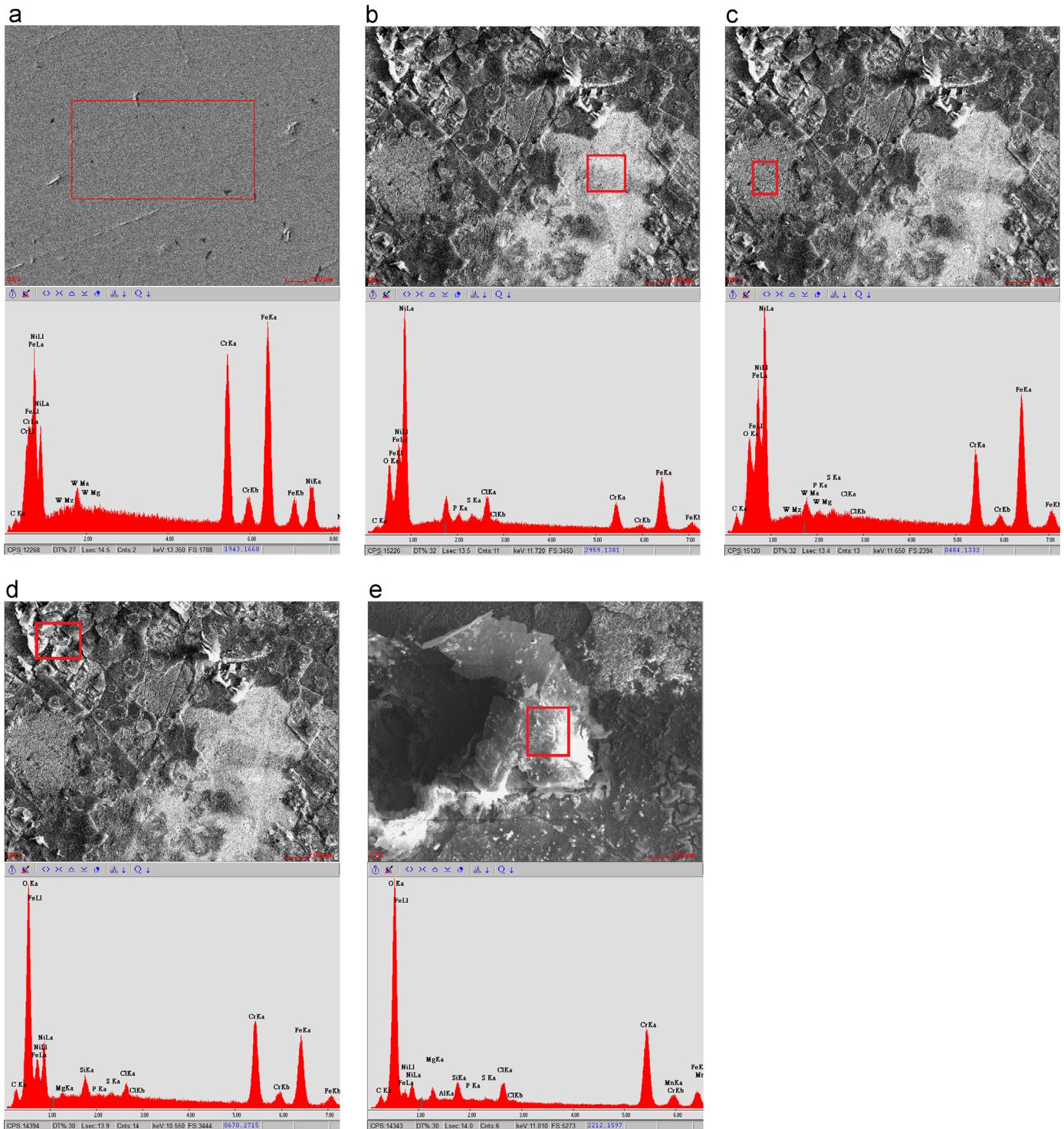


Fig. 7. FESEM-EDX surface analysis of SS310 non-corroded (a) and corroded (b), (c), (d), and (e) in 34.42 wt% NaCl – 65.58 wt% LiCl at 650 °C showing different regions analyzed.

no longer protective. Then, the Cl is liberated and will again attack the Cr, leaving the bulk of the alloy depleted from this key protective element.

The presence of oxides as corrosion products is evidence that elemental oxygen or containing compounds were present during the corrosion process. We used untreated salts because for economic consideration CSP plants might not be able to employ purification processes. Currently nitrate molten salts are not further treated in current CSP operating plants. It is expected that

controlled chemistry of the salts will be required in order to mitigate corrosion in chloride molten salt systems. Because untreated salts will have moisture, oxygen and/or oxides present, corrosion levels are expected to be high.

Comparing the baseline composition of In800H (Fig. 8(a)) with the light phase shown in Fig. 8(b) and (d), it is clear that Cr was also depleted in In800H. The dark phase (Fig. 8(c)) was identified as a mixed Ni-Cr-Fe-Mn oxide with small amounts of Ti. The dark-phase morphology observed in Fig. 8(e) was identified as the same

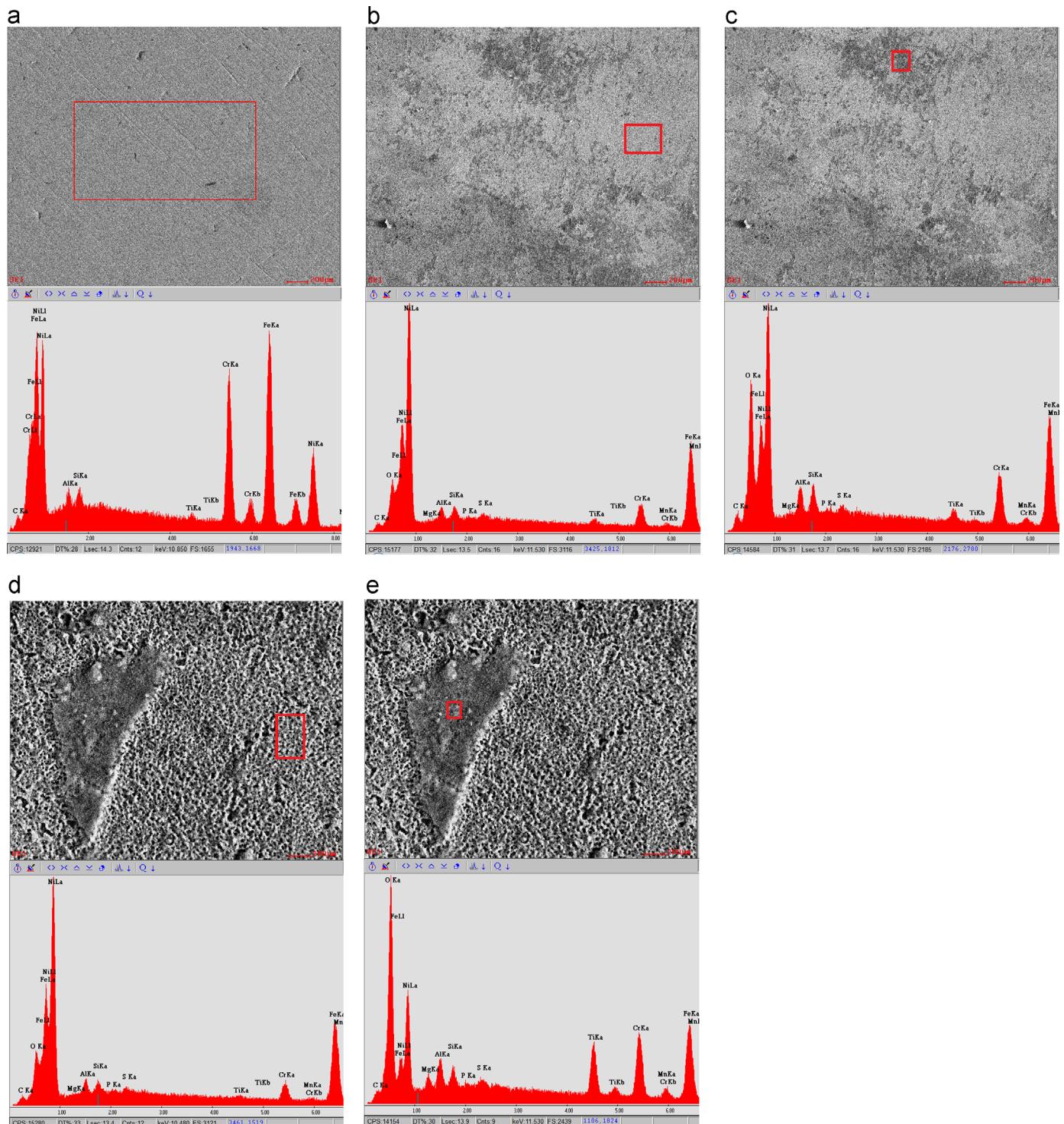


Fig. 8. FESEM-EDX surface analysis of In800H non-corroded (a) and corroded (b), (c), (d), and (e) in 34.42 wt% NaCl – 65.58 wt% LiCl at 650 °C showing different regions analyzed.

mixed-oxide phase, but enriched in Ti. After FESEM and EDX analyses, it may be suggested that the corrosion mechanism of In800H is similar to the one identified for SS310.

Metallographic characterization of nickel superalloy IN625 (see Fig. 6(e), f, 9) reported surface degradation and precipitation of secondary phases. The EDX spectrum of IN625 (Fig. 9(c) and (d)) showed the presence of small amounts of Cl, which indicates that warm deionized water did not fully remove salt from the surface of the sample after the corrosion test. The surface analyzed in Fig. 9(b) showed a very low amount of Cr compared to the baseline

composition (Fig. 9(a)), suggesting that this element was also depleted at the surface during corrosion. EDX reported the presence of Cr-Fe-enriched oxide in this region. Fig. 9(c) shows a granular light phase consisting of Ni oxide with small amounts of Cr and Fe. The needle-type morphology shown in Fig. 9(d) was reported to be Cr oxide. Fig. 6(f) shows a higher magnification of the IN625 surface. Based on the corrosion rates reported for this alloy and the surface analysis, we suggest that this alloy is more corrosion resistant to molten chloride than high-steel alloys. Intergranular or pitting corrosion could be possible, but needs to be confirmed

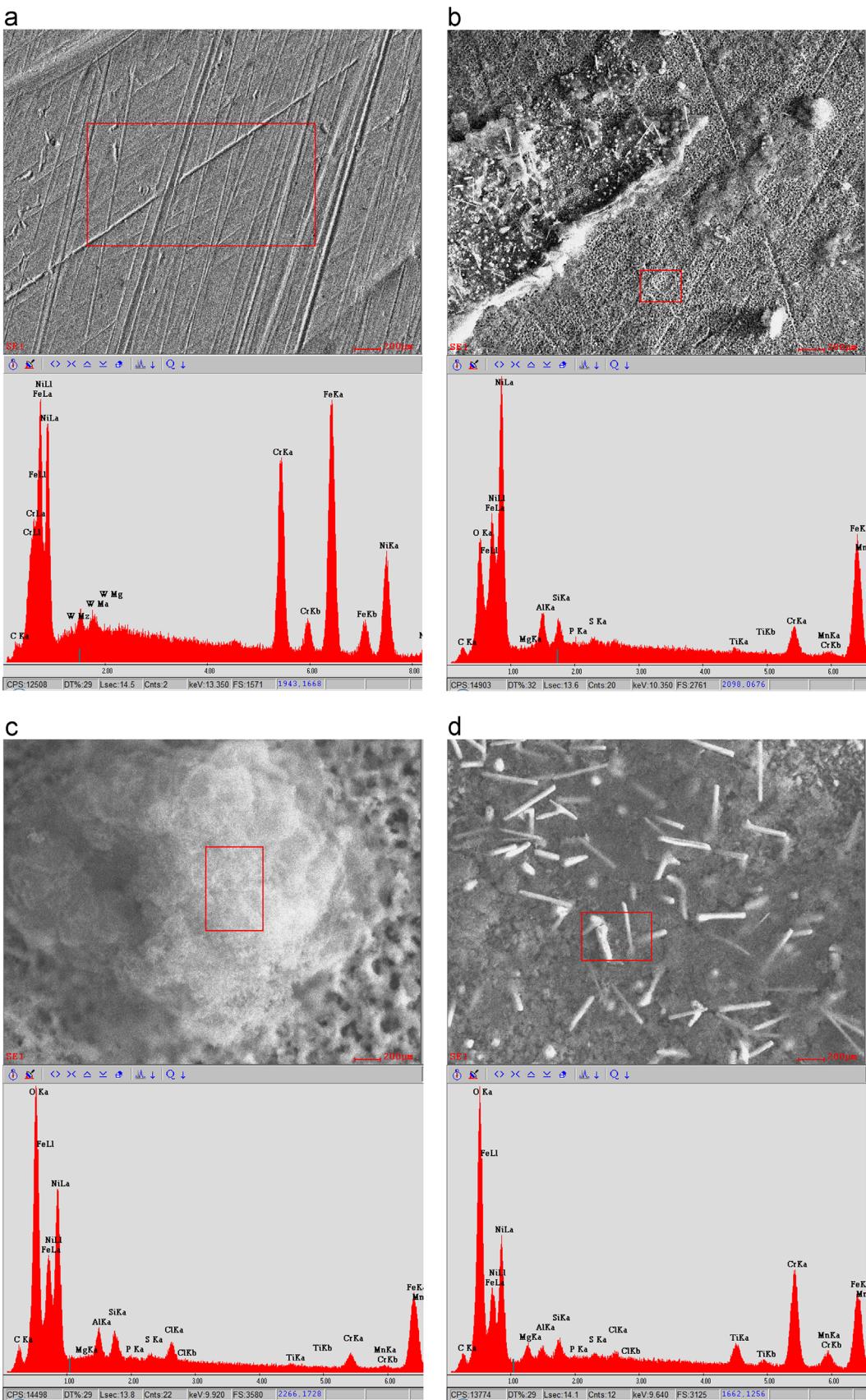


Fig. 9. FESEM-EDX surface analysis of IN625 non-corroded (a) and corroded (b), (c), and (d) in 34.42 wt% NaCl - 65.58 wt% LiCl at 650 °C showing different regions analyzed.

Table 4.

ICP-MS chemical analysis of dissolved elements from Aremco 645-N cement with BN film on top into the molten 34.42 wt% NaCl – 65.58 wt% LiCl at 650 °C.

Elemental Composition (average ± standard deviation) [ppm]											
Al	B	Ca	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	V
0.19 ± 0.04	1.43 ± 1.01	bdl ^a	0.23 ± 0.06	0.20 ± 0.05	0.34 ± 0.17	0.53 ± 0.14	0.67 ± 0.55	0.24 ± 0.06	bdl ^a	bdl ^a	0.18 ± 0.05

^a bdl: below detection limit.

Table 5.

ICP-MS chemical analysis (average ± standard deviation) of baseline and dissolved elements from alloys into the molten 34.42 wt% NaCl – 65.58 wt% LiCl.

Test	Elemental Composition [ppm]			
	Cr	Mn	Fe	Ni
Baseline	0.16	0.16	0.73	0.49
650 °C				
SS310	4.08 ± 2.31	0.93 ± 0.17	12.07 ± 3.15	4.05 ± 0.52
In800H	1.50 ± 0.60	0.52 ± 0.26	2.76 ± 0.84	3.87 ± 0.30
IN625	0.91 ± 0.39	bdl ^a	1.93 ± 0.69	3.96 ± 0.49
700 °C				
SS310	5.22 ± 2.62	3.51 ± 1.43	66.01 ± 44.95	2.25 ± 0.07
In800H	1.79 ± 0.10	2.55 ± 1.53	36.46 ± 22.58	2.62 ± 0.90

^a bdl: below detection limit.

with further cross-section analysis of the corroded samples.

ICP-MS chemical analysis of the salt was performed to the cement dissolution test, before the corrosion test to determine the baseline, and after each alloy's corrosion test. Table 4 shows the composition of elements dissolved from the cement to the molten chloride after two hours of exposure. Values are low (below 0.7 ppm) with the boron with the highest concentration (1.43 ppm). Elemental boron comes from the BN film that was sprayed to the surface of the cured cement. The low concentration of elements in solution shows the chemical stability of the cement exposed to the molten chloride. These values were used to correct the measurements obtained for the alloys corrosion tests.

The composition of the baseline and the corroded and dissolved elements into the molten salt is shown in Table 5. Some results have a large standard deviation, and our comparison considered the observed trends. In general, the amount of Cr, Mn, and Fe dissolved into the molten salt at 650° and 700 °C increased in the following order: IN625 < In800H < SS310. These results corroborate the corrosion rates obtained from the electrochemical tests, in which the corrosiveness behavior of the alloys increased in the same order. IN625 is the most corrosion-resistant alloy against molten NaCl–65.58 wt% LiCl. When the corrosion temperature is increased, more Cr, Mn, and Fe are dissolved into the molten salt from the alloys. Dissolution of nickel does not follow a clear trend with the alloy's composition or corrosion temperature, and the results for this element are non-conclusive.

4. Conclusions

The corrosion behavior of the tested alloys (SS347, SS310, In800H, and IN625) in molten 34.42 wt% NaCl – 65.58 wt% LiCl at 650° and 700 °C showed active corrosion under an imposed anodic potential. The alloy with the highest corrosion rate of 7.49 ± 0.32 mm/year was SS347. This alloy has a very low nickel content of only 9.62 wt%, and higher nickel concentration is required for corrosion-resistance behavior against molten chloride

systems.

In800H performed slightly better than SS310; however, both alloys exhibited localized (intergranular or pitting) corrosion. This type of corrosion is very common in chloride systems, and the failure of the alloys can be catastrophic.

IN625, a nickel superalloy (> 58 wt% Ni) with a very low amount of iron (< 5 wt% Fe), was the most corrosion-resistant alloy against molten NaCl–LiCl at 650 °C, with a corrosion rate of 2.80 ± 0.38 mm/year.

EDX analyses corroborated that chromium and iron were preferentially corroded from SS310, In800H, and IN625. Corrosion tests of SS310 resulted in Cr oxide and mixed oxides enriched in Ni with small amounts of Fe and Cr. For In800H, the presence of Ni-Cr-Fe-Mn-Ti was observed. IN625 showed the presence of Cr-Fe oxide. Different oxide morphologies were resolved. Granular oxide morphology consisted of Ni oxide with small amounts of Cr and Fe. The needle-type morphology was identified to be Cr oxide. The corroded surface of IN625 showed some extent of localized corrosion, but lower than in SS310 and In800H. These results indicate that oxygen contamination to the salts could have been causing a large portion of corrosion. In the presence of oxygen, the alloy forms oxides that eventually dissolve into the molten chloride salt liberating the oxygen component which then later is able to keep the oxidation process going. It is expected that in an oxygen-free system less corrosion products would be transported, less cathodic reactions will be in place (oxidizer effect) and thus less corrosion will occur. This must be confirmed with further evaluations using highly purified salts.

ICP-MS analysis of the salts after corrosion showed that, in general, the amount of Cr, Mn, and Fe dissolved into the molten salt at 650° and 700 °C increased in the following order: IN625 < In800H < SS310. These results corroborate the corrosion rates obtained from the electrochemical tests in which the susceptibility to corrosion of the alloys increased in the same order.

When the corrosion temperature increased from 650° to 700 °C, more Cr, Mn, and Fe were dissolved from the alloys into the molten salt. An increase in temperature of as little as 50 °C more than doubled the corrosion rates of In800H and SS310 compared to the initial 650 °C test.

For TES applications, corrosion rates with magnitudes of a few millimeters per year cannot be sustained. Corrosion rates of molten-salt containment alloys should be lower than 50 µm/year. Additionally, localized corrosion (intergranular or pitting) can be catastrophic. Thus, corrosion-mitigation approaches are required for advanced CSP plants to meet DOE SunShot targets.

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