Investigation on the Corrosion Behavior of Nickel-Base Alloys in Molten Chlorides for Sensible Heat Energy Applications

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Nine selected alloys are exposed in molten KCI–LiCl (eutectic composition) at 1073 K for 167 h under argon atmosphere to predict the long-term corrosion behavior of these structural materials. The corrosive attack of each alloy is assessed with gravimetric methods, scanning electron microscopy, and energy-dispersive X-ray spectroscopy measurements. The corrosion rate of each alloy is calculated in accordance with ASTM G1-03. Low chromium containing alloys as HAYNES 242, Hastelloy B-3, and Hastelloy N revealed minor or no significant corrosive attack after molten chloride exposure. Alloy 600, Alloy 617, HAYNES 625, Hastelloy X, HAYNES 230, and HAYNES 188 with a chromium content wCr > 8% show severe corrosive attack with complete chromium depletion along the near-surface layer and partially along grain boundaries. The results show that chromium forms chromium oxide with impurities of oxygen and water vapor at low oxygen partial pressures. This initiates an accelerated corrosion of the alloying elements in the matrix of Ni, Cr, Mo, Fe, and Co, due to chlorine formation. The influence of the composition of nickel-base alloys on the corrosion resistance is discussed based on the comparison of the gravimetric measurements and thermodynamic calculations.

1. Introduction

Molten salts are increasingly applied as heat-transfer fluids in concentrated solar power (CSP) systems, as well as in Nuclear Energy Gen IV reactor concepts, because of their wide liquid-phase temperature range and low vapor pressure at higher temperatures. State-of-the-art molten nitrates are applied in operational large-scale CSP power plants (e.g., Gemasolar, Crescent Dunes, and Shouhang Dunhuang) because of their low melting point (∼493 K), but they decompose at around 833 K and are, therefore, not applicable for temperatures above that level.[1] To increase efficiency of CSP applications and enable heat transport and storage at higher temperatures, molten chlorides are being considered to fulfill these requirements at salt investment costs at the same level as molten nitrates.[2]

The SunShot Initiative of the Department of Energy (USA) addresses the goal of an operation temperature at 1023 K to significantly increase CSP system efficiency and achieve electricity generation costs below 0.06 $ kWh−1.[3] As molten chlorides, along with molten fluorides, are known to show higher corrosion rates than molten nitrates, material research is conducted to assess corrosion behavior of construction materials. For CSP applications, it is estimated that a target material corrosion rate below 20 μm per year is needed to achieve a system service life of 30 years.[4] Molten chlorides are already applied for the extraction of metals, heat treatment of alloys in steel industry, and for pyrochemical reprocessing of spent nuclear fuel.[5,6] The application of molten chlorides for energy applications requires an evaluation of the corrosive attack of structural materials due to different application conditions such as temperature level, atmosphere, and exposure time of components.

Among the relevant eutectic chloride salt mixtures for high-temperature heat transport and storage, this study focuses on the corrosion behavior of a eutectic mixture of LiCl and KCl (xLiCl = 59%; xKCl = 41%). Although KCl–LiCl comes with higher investment costs (∼9.50 € kg−1) compared with eutectic mixtures of ZnCl2, KCl, MgCl2, or NaCl (∼0.5–1.0 € kg−1), it shows thermal stability and low vapor pressures at target temperature of 1073 K and a melting temperature of 628 K.[7,8] Moreover, mixtures containing MgCl2 are known to form undesirable MgO when dried after moisture exposure which enables a considerable change in thermodynamic media properties over time.[9]

As stated earlier, structural materials for the application of molten chlorides as heat-transfer media require high oxidation resistance along with mechanical strength at high temperatures.
In the 1960s and 1970s, nickel-base alloys were extensively investigated and further developed throughout the molten salt reactor experiment (MSRE) at Oak Ridge National Laboratory (ORNL) to withstand oxidizing atmospheres of LiF–BeF₂ (FLiBe) and LiF–NaF–KF (FLiNaK) as liquid-phase coolant salt at a temperature level of 1073 K or above. These material studies on the MSRE indicate that high mass contents of nickel and low contents of chromium are desirable for the selection of long-term resistant construction materials, because chromium is the least noble of the alloying elements that faces severe selective attack and depletion.[10]

Along with increasing research activities on molten chlorides as heat-transfer fluid in CSP applications in the last decade, material research is necessarily conducted to assess corrosion resistance of structural materials and develop corrosion mitigation strategies as active corrosion inhibition or coatings. This study focuses on the comparison of the corrosion behavior of nickel-base alloys in molten chlorides at similar test conditions. Therefore, selected alloys were exposed in KCl–LiCl (eut.) at 1073 K for 167 h to predict long-term corrosion behavior of potential structural materials.

2. Experimental Section

2.1. Preparation of Alloy Specimens

Selected nickel-base and cobalt-base alloys shown in Table 1 were tested in the present study. The mass composition of each alloy was measured using energy-dispersive X-ray spectroscopy (EDX) (Phenom ProX Desktop scanning electron microscope [SEM]). Specimens with a size of 1.5 · 8.0 · 20.0 (mm) of each alloy were fabricated and polished with 8.4 μm SiC abrasive paper in order to ensure comparability between the alloys and increase homogeneity of the surface. To maximize the exposed surface to the molten salt and does not contribute additional elements to the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate. The test setup allows constant argon atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction.

As shown in Figure 1, each alloy specimen bend (1) was positioned centric in a nickel crucible (2) of size 35 mm diameter, 35 mm height (wNi = 99.35%), and filled to the brim with around 30 g KCl–LiCl (eut.) to ensure full specimen wetting after volume reduction in the melting process. A nickel crucible was chosen because pure nickel is indicated not to interact with the molten salt and does not contribute additional elements to the investigated system.[2,13] Filled crucibles were placed in a steel container (3) to control the test atmosphere and maintain corrosion protection of the furnace (4). Argon was chosen as test atmosphere because of its inert and stable behavior at a temperature of 1073 K and due to the necessity to exclude oxygen from the reaction. Oxygen as an impurity is reported to significantly affect the corrosion reaction and therefore increases the corrosion rate.[14] The test setup allows constant argon flow (5) (purity ≥ 99.999%, <3 ppm H₂O) through the test container that is controlled by a mass-flow controller (6) (Bronkhorst El-Flow F-201AC). Argon gas and salt vapor were constantly released in the exhaust through an outlet pipe (7).

![Figure 1](image-url)
2.3. Experimental Procedure

After inserting the container filled with specimens in the furnace, the volume flow of argon for all test series was set at 0.09 m³ h⁻¹. As the loading process of the container and the furnace allows moisture to access the system, furnace temperature was initially set at 413 K and held for 4 h to regain water and oxygen-free atmosphere in the container. After drying process, the temperature was raised to the test level of 1073 K with a heat-up rate of ≈20 K min⁻¹ and then held for 167 h. After 167 h exposure time, the furnace was switched off and argon flow was continued until the entire setup reached room temperature. The crucibles then were removed from the container and specimens were cleaned in deionized water in accordance with ASTM G1-03 cleaning procedure. The cleaned specimens were analyzed with mass change measurement (Ohaus Adventurer AR0640, accuracy of 0.1 mg) and subsequently cross-sectional cut in the polished section, cold mounted and polished for metallographic analysis with SEM/EDX measurement.

3. Results and Discussion

3.1. Mass Loss and Corrosion Rate Determination

The specific mass loss Δmᵢ in mg·cm⁻² is quantified with the overall specimen mass loss divided by the LSM-detected surface area before exposure of each specimen. As incorporated in ASTM G1-03 regulations, the corrosion rate (CR) in μm·per year then is calculated according to Equation (1), with a constant (K) of 8.76 × 10⁻⁵, detected mass loss (W) in grams, and specimen surface area (A) in cm². The value of exposure time (T) in hours and specific density (D) in g·cm⁻³ are constant for tested materials.¹⁵

\[ CR = \frac{K \cdot W}{A \cdot T \cdot D} \]  

(1)

The maximum depletion depth of chromium was measured by the mapping of the chromium distribution on each alloy sample cross-cut section with EDX-analysis as shown in Section 3.2. The combined test results of all test series are given in Table 2 and arranged in the order of detected specific mass loss.

Table 2. Corrosion of nickel-base alloys after 167 h exposure in KCl–LiCl (eut.) at 1073 K.

| Material     | UNS number | Relative mass loss of specimen in [%] | Specific mass loss in mg·cm⁻² | Calculated corrosion rate in [μm·per year] (ASTM G1-03) | Maximum chromium depletion depth in [μm] |
|--------------|------------|-------------------------------------|-----------------------------|-------------------------------------------------------|----------------------------------------|
| HAYNES 188  | R 30188    | 5.09 ± 0.79                         | 15.69 ± 0.54                | 917 ± 32                                              | 318                                    |
| HAYNES 230  | N 06230    | 3.85 ± 0.22                         | 12.48 ± 0.14                | 730 ± 8                                               | 328                                    |
| Hastelloy X | N 06002    | 4.72 ± 0.03                         | 10.74 ± 1.29                | 685 ± 8                                               | 165                                    |
| HAYNES 625  | N 06625    | 3.46 ± 0.78                         | 10.56 ± 1.38                | 656 ± 8                                               | 106                                    |
| Alloy 617   | N 06617    | 2.08 ± 0.47                         | 06.14 ± 0.19                | 383 ± 12                                              | 271                                    |
| Alloy 600   | N 06600    | 2.62 ± 0.27                         | 05.07 ± 0.53                | 316 ± 33                                              | 274                                    |
| Hastelloy N | N 10003    | 0.02 ± 0.17                         | 00.00 ± 0.51                | 0 ± 31                                                | 35                                     |
| Hastelloy B-3 | N 10675   | 0.48 ± 0.48                         | 01.11 ± 1.11                | –                                                    | –                                      |
| HAYNES 242  | N 10242    | 0.85 ± 0.25                         | 02.42 ± 0.70                | –                                                    | –                                      |

The tested alloys show different mass losses that can be attributed to only element composition. Although chromium is known to be severely attacked in molten salts, other alloying elements as nickel, molybdenum, cobalt, and iron influence the corrosive attack, as the values of the specific mass loss/chromium content plot (Figure 2) are scattered. Considering nickel as a highly resistant alloying metal in molten chlorides, the nickel content is also not linearly dependent on the specific mass loss as detected for Alloy 600 (Table 2). The comparison of the materials Alloy 617 (w_Cr = 20.2%; w_Ni = 53.7%) and Alloy 600 (w_Cr = 14.3%; w_Ni = 76.7%) shows that although Alloy 617 is expected to show higher mass loss, it did not face disproportionate higher mass loss along with an equal chromium depletion depth. First, this indicates that the refractory metal molybdenum can increase corrosion resistance as also detected for HAYNES 242, Hastelloy B-3, and Hastelloy N that contain molybdenum w_Mo between 19% and 31%. This is affirmed by the comparison of HAYNES 625, Hastelloy X, HAYNES 188, and HAYNES 230 (w_Cr ≈ 19%), because HAYNES 625 and Hastelloy X (w_Mo ≈ 11%) showed lower corrosion rates than HAYNES 188 and HAYNES 230 (w_Mo < 2.5%).

![Figure 2. Mass loss dependency of chromium content of tested nickel-base alloys after 167 h exposure in KCl–LiCl (eut.) at 1073 K.](image)
Second, it is indicated that the matrix of the alloy as the grain size also has a significant influence on the corrosion rate, because with an increasing depth under the surface, chromium depletes particularly along the grain boundaries (as detected in Section 3.2). In corrosion studies on molten fluorides, chromium depletion is increasingly measured with decreasing alloy grain sizes.\textsuperscript{16}

The alloys Hastelloy B-3 and HAYNES 242 with a chromium content $w_{\text{Cr}}$ below 8% showed mass gain after exposure that is also reported for nickel-base alloys exposed to molten fluorides at 1253 K.\textsuperscript{17} The calculation of the corrosion rate was not applied for these materials. Hastelloy N specimens showed both mass loss and mass gain with chromium depletion under the surface.

In compliance with required CSP corrosion rate below 20 μm·per year, HAYNES 242, Hastelloy N, and Hastelloy B-3 are detected to meet these requirements at 1073 K under the mentioned examination conditions.

### 3.2. Cross-Section Images of Specimen after Exposure

The cross-section SEM/EDX images (Figure 3–10, and 11) were measured with an accelerating voltage of 15 kV (Phenom ProX Desktop SEM). Linescan measurements of the alloy composition along the marked measurement line are smoothened with moving average value of 10 data points and aligned with the surface level of the corresponding SEM/EDX measurements. The figures show the corrosive attack of the subsurface alloy matrix that is characteristic for each alloy. Phenomenologically, HAYNES 188 (Figure 3), Alloy 230 (Figure 4), and Alloy 617 (Figure 7) cross sections reveal intergranular corrosion at the attacked grain boundaries associated with chromium depletion. Furthermore, the alloys Alloy 617, HAYNES 188, HAYNES 230, HAYNES 625 (Figure 6), Hastelloy N (Figure 9), and Hastelloy X (Figure 5) show voids along the near-surface area (17–160 μm) as pitting corrosion damage, which is less pronounced at Alloy 600. Hastelloy X (Figure 5) showed voids within the alloy matrix indicated as micro-channels with no perpendicular connection to the surface layer.

The EDX measurements of the chromium distribution and the line scans of HAYNES 188, HAYNES 625, Hastelloy N, Hastelloy X, and Alloy 617 show that chromium was only depleted along the void-layer. For HAYNES 230 and Alloy 600, chromium depletion of the alloy matrix was detected in...
Figure 5. Cross-section SEM image (left), line scan measurement (middle), and EDX chromium distribution (right) of Hastelloy X after 167 h exposure in KCl–LiCl (eut.) at 1073 K.

Figure 6. Cross-section SEM image (left), line scan measurement (middle), and EDX chromium distribution (right) of HAYNES 625 after 167 h exposure in KCl–LiCl (eut.) at 1073 K.

Figure 7. Cross-section SEM image (left), line scan measurement (middle), and EDX chromium distribution (right) of Alloy 617 after 167 h exposure in KCl–LiCl (eut.) at 1073 K.
Figure 8. Cross-section SEM image (left), line scan measurement (middle), and EDX chromium distribution (right) of Alloy 600 after 167 h exposure in KCl–LiCl (eut.) at 1073 K.

Figure 9. Cross-section SEM image (left), line scan measurement (middle), and EDX chromium distribution (right) of Hastelloy N after 167 h exposure in KCl–LiCl (eut.) at 1073 K.

Figure 10. Cross-section SEM image (left), line scan measurement (middle), and EDX chromium distribution (right) of Hastelloy B-3 after 167 h exposure in KCl–LiCl (eut.) at 1073 K.
visually unaffected depths. The line scans of the least attacked alloys Hastelloy B-3 (Figure 10) and HAYNES 242 (Figure 11) show a slight decrease in molybdenum content under the surface, whereas a decrease in chromium is not detected. None of the SEM/EDX measurements applied on the specimens in initial state or as shown after exposure revealed an indication of an oxide scale. This is due to the limitation of the SEM/EDX measurement method resolution for the direct measurement of an oxide scale with a thickness in nanometer scale. Also, no chloride residues were found because of equivalent measurement limitations and specimen-cleaning procedure might have dissolved corrosion products in the deionized water.

3.3. Thermodynamic Considerations

Corrosion is defined as an irreversible electrochemical process and can be described as an electrochemical half-cell reaction. In an alloy, the anodic reaction causes the release of metal atoms (M) to form a metal cation (M\(^{n+}\)) and an equivalent number of electrons (e\(^{-}\)) (oxidation reaction) (Equation (2)). In a cathodic reaction as a reduction reaction, an oxidant consumes electrons and forms a reductant (Equation (3)). The overall reaction is given in Equation (4).\(^{[18]}\)

Anodic Reaction : \[ M \rightarrow M^{n+} + ne^{-} \]  
Cathodic Reaction : Oxidant + ne\(^{-}\) \rightarrow Reductant 
Overall Reaction : \[ M + \text{Oxidant} \rightarrow M^{n+} + \text{Reductant} \]

As an alloy surface consists of an array of metal phases and grain boundaries, coupled half-cell reactions can occur on the same metal surface due to different energy levels of the atoms in the grain structure. In presence of an electrolyte, released metal cations dissolve and form corrosion intermediates or products.\(^{[18]}\)

Molten chloride corrosion can therefore be described as an electrochemical half-cell reaction due to the electrolytic behavior of molten salts.\(^{[19]}\) The corrosion reaction influences the matrix of alloys by uniform thinning, pitting, and internal corrosion or intergranular attack.\(^{[5]}\) Considering the free energy for the formation of chlorides of the main alloying elements Ni, Cr, Mo, Co, and Fe as the driving force of molten chloride corrosion reactions, the molten salt components KCl and LiCl show a more negative free energy, i.e., for MoCl\(_2\), NiCl\(_2\), and CoCl\(_2\) (Figure 12). Thus, alloying elements or dissolved cations of these elements thermodynamically do not further corrode or form metal chlorides when the equilibrium state with the molten salt is reached.\(^{[6,10]}\)

The detected corrosion influence on the specimen’s surface did not only obey a thermodynamically induced formation of metal chlorides under uniform discharge metal ions thereof, as detected in HAYNES 188 specimens. The occurrence of voids and grain boundary attack detected in this study implies a more complex reaction mechanism of molten chloride corrosion. Studies on the corrosion of molten salts propose an impurity-driven model for the corrosion mechanism of molten chlorides.\(^{[7,10,20]}\) Water and/or oxygen as impurities primarily impact corrosion, as they

![Figure 11. Cross-section SEM image (left), line scan measurement (middle), and EDX chromium distribution (right) of HAYNES 242 after 167 h exposure in KCl–LiCl (eut.) at 1073 K.](image)

![Figure 12. Gibbs free energy of formation for selected metal chlorides taken from FactSage SGPS database.](image)
can form intermediate oxides that interfere with cations from the electrochemical anodic discharge of the main alloying elements (Ni, Cr, Mo, Co, and Fe) that are considered in this study. The experimental setup (Figure 1) of this study is aimed to minimize the effect of impurities. However, as the alloys in their initial state form thin oxide layers and the flowing inert gas argon contains small amounts of oxygen and water vapor, these impurities can initiate impurity-driven corrosion that can significantly affect the corrosion mechanism of structural materials. Water vapor at high temperatures enables, i.e., hydrolysis or/and other reactions that produce O²⁻ ions and HCl (Equation (5)) that completely dissolve in a melt. The solubility of oxygen, chlorine, hydrogen chloride, and water vapor is reported by Ozeryanaya to be low in molten alkali and alkaline-earth chlorides with a solubility constant $K_p$ of $10^{-8}$ mol cm$^{-3}$ for oxygen and a solubility constant of water vapor in KCl–LiCl at 663–753 K in the same order. However, it can be assumed that oxygen-containing species were dissolved continuously in the melt due to a constant cover gas inflow in the test container as used in this study.

$$\text{H}_2\text{O(g)} + 2\text{Cl}^- \leftrightarrow \text{O}^{2-} + 2\text{HCl(g)} \quad (5)$$

These dissolved O²⁻ ions can form a metal oxide scale on the alloy surface by a reaction with the alloying elements. The propagation of the oxide scale formation is dependent on the partial pressure of oxygen on the surface and the thermodynamic tendency of an element to form an oxide. These oxide layers then can further react with the molten salt constituents and produce chlorine.

The release of chlorine enables an accelerated formation of metal chlorides in different phases depending on the temperature and solubility. As the initial formation of metal oxides was not detected in this study, further thermodynamic considerations focus on the formation reaction of metal chlorides.

The reaction is thermodynamically quantified by the free Gibbs energy change ($\Delta G$) with the number of exchanged electrons ($n$), the Faraday constant ($F$), and the electrode potential ($E$) (Equation (6)).

$$\Delta G = -nFE \quad (6)$$

As suggested by Guo et al., the following half-cell reactions should be considered for the formation of metal chlorides:

$\text{Cl}_2 + \text{n}e^- \leftrightarrow \text{nCl}^- \quad (7)$

$\text{M} + \text{nCl}^- \leftrightarrow \text{MCl}_n + \text{n}e^- \quad (8)$

Reaction (7) and (8) result into the overall reaction (Equation (9)).

$$\text{M} + \frac{n}{2}\text{Cl}_2 \leftrightarrow \text{MCl}_n \quad (9)$$

Based on Equation (9), Gibbs free energy of formation was calculated for the most stable phases using FactSage SGPS database for potential chlorides of Ni, Mo, Co, Fe, and Cr. The results of these calculations are plotted in Figure 13. As detected in this work, as well as reported in other published studies on corrosion of structural materials in molten chlorides and molten fluorides, the alloying element chromium is severely attacked in molten salts at elevated temperatures.

Studies of Li et al. focusing on the corrosion kinetics of pure Cr in KCl at 923 K under air atmosphere detect the occurrence of voids and cracks in the structure of the chromium specimen that is caused by the evaporation of volatile reaction intermediates as CrCl$_3$. Chromium oxide formation (Cr$_2$O$_3$) was measured as dominant corrosion product, and the formation of chromates K$_2$CrO$_4$ (Equation (10)) and K$_2$Cr$_2$O$_7$ was found to occur at lower rates. As all these reactions release chlorine, they consequently initiate the penetration of the metal surface by accelerating metal chloride formation.

$$4\text{KCl(g)} + \text{Cr}_2\text{O}_3 + \frac{5}{2}\text{O}_2 \rightarrow 2\text{K}_2\text{CrO}_4 + 2\text{Cl}_2 \quad (10)$$

Thermodynamically, Cr$_2$O$_3$ can be formed at lower O²⁻ concentration compared with e.g., NiO (Figure 14a) and thus can influence corrosion of the alloy at low oxygen partial pressures ($p_{O_2} \geq 10^{-27}$ bar). The reaction of chromium oxide and the molten chlorides increases the local partial pressure of Cl$_2$. A uniform passivation layer of chromium oxide does not form, so the metal surface is constantly attacked by chlorine and corrosion intermediates and/or products constantly form and dissolve in the melt.

Compared with the alloying elements Ni, Mo, Fe and Co, chromium predominantly forms chlorides at relatively low partial pressure of chlorine ($p_{Cl_2} \geq 10^{-13}$ bar). Furthermore, at constant chlorine concentration, chromium is more prone...
to chloride formation, due to the most negative Gibbs energies of formation as shown in Figure 13. Both of these indications lead to an accelerated depletion of chromium that is dependent on the concentration of impurities in the system and the chromium concentration in an alloy. As the impurity concentration in the flowing cover gas (purity ≥ 99.999%, < 3 ppm H₂O) and solubility of these impurities in the molten chloride is equal for all tested materials in this study, SEM/EDX images (Section 3.2) indicate that the content of chromium in an alloy is crucial for the propagation of chromium oxide layer formation accompanied by the formation of volatile chromium chlorides and their resulting voids as detected for HAYNES 188 (Figure 3), HAYNES 230 (Figure 4), Hastelloy X (Figure 5), HAYNES 625 (Figure 6), Alloy 617 (Figure 7), Alloy 600 (Figure 8), and Hastelloy N (Figure 9). These volatile corrosion reaction products, in particular those in gaseous phase were carried out of the system by the continuous cover gas flow, so no equilibrium state is reached.

In studies by Ruh et al., pure nickel covered with ZnCl₂–KCl in argon atmosphere containing 8 vol% oxygen at 593 K, nickel corroded less severely in comparison to iron and chromium. At 1073 K, it is indicated that nickel requires a relatively high oxygen concentration (pO₂ > 10⁻¹⁴ bar) to form NiO (Figure 13a). Below this level, nickel predominantly forms solid phase NiCl₂ at a partial pressure pCl₂ > 10⁻⁷ bar and smaller quantities of nickel oxides, because their stability is thermodynamically low.[6,28] Both of the aforementioned studies indicate that nickel is the most resistant element to oxide and chloride formation when exposed to molten chlorides.

In addition, nickel chlorides show the highest Gibbs free energies of formation among all considered corrosion species (Figure 13). The mass losses measured in this study behaved in accordance to the mass loss of other published research, as alloys with higher contents of nickel have the tendency to show fewer mass loss on molten chloride corrosion.[5]

Molybdenum was shown to be resistant in the studies of Karpov et al. in chloride melts at 1023 K after 30 h exposure. For molybdenum chloride formation, it can be stated that with an increasing temperature, solid molybdenum chlorides decompose into a gaseous phase and solid lower molybdenum chlorides. MoCl₃ decomposes into solid MoCl₂ and gaseous MoCl₄ at around 680 K and solid MoCl₂ as the most stable molybdenum chloride decomposes into solid Mo and gaseous MoCl₄ at 780 K.[29–31] It can be inferred that at temperatures over 780 K, molybdenum is decreasingly affected by chlorine attack. Although molybdenum predominantly forms oxides at relatively low oxygen concentrations (pO₂ > 10⁻¹⁹ bar) compared with nickel, it is thermodynamically more resistant to chloride formation (pCl₂ > 10⁻⁷ bar) (Figure 14b). This is considered an additional reason for the higher corrosion resistance of alloys with high molybdenum contents, such as HAYNES 242, Hastelloy B-3, and Hastelloy N, detected in this study.

Figure 14. Merged predominance phase diagrams at 1073 K of Cr–O₂–Cl₂ and a) Ni–O₂–Cl₂, b) Mo–O₂–Cl₂, c) Fe–O₂–Cl₂, d) Co–O₂–Cl₂ calculated with FactSage SGPS and SGTE database.
As reported by Ruh et al., pure iron shifts from the predominant formation of iron chloride in an incubation period to predominant formation of iron oxide while exposed to ZnCl2–KCl (eut.) in argon with 8 vol% O2 at 593 K. This is accompanied by chlorine release at the iron oxide scale and results into a constant mass loss over time.\(^\text{28,32}\) As shown in Figure 14c, at 1073 K, an iron oxide scale is predominantly formed at a local oxygen partial pressure of \(p_{O_2} > 10^{-20}\) bar. Equivalent to Equation (10), the formed iron oxide scale reacts with the alkali chloride under chlorine release\(^\text{33}\)

\[
2\text{KCl} + \text{Fe}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{K}_2\text{Fe}_2\text{O}_4 + \text{Cl}_2
\]  

\(\text{(11)}\)

At a local chlorine partial pressure of \(p_{Cl_2} > 10^{-10}\) bar, liquid-phase \(\text{FeCl}_3\) is predominantly formed that is found to be highly volatile and dissolve from the alloy matrix in the molten chloride.\(^\text{14}\) In addition, a study of Cha and Spiegel on iron in KCl systems states that KCl can form eutectics with nascent \(\text{FeCl}_2\) and \(\text{FeCl}_3\) with a melting temperature below 493 K (KCl–FeCl3) or below 666 K (KCl–FeCl2).\(^\text{33}\) This explains the extensive layer of voids detected in the Hastelloy X (Figure 5) cross-section SEM image compared with the other alloys tested. Considering similar quantities of iron \(w_{Fe} = 18.2\%\) and chromium \(w_{Cr} = 19.8\%\) for Hastelloy X, the formation of chlorine induced by iron chloride formation is indicated to also accelerate iron chloride formation and that causes extensive in-grain corrosion, respectively. This indication seems valid, because line scans of Alloy 600 \(w_{Fe} = 8.1\%\), HAYNES 625 \(w_{Fe} = 4.3\%\), and Hastelloy N \(w_{Fe} = 3.8\%\) do not show significant iron depletion under specimen’s surface and similar alloy matrix attack.

Cobalt, along with refractory metals in the alloy, is reported to reduce diffusion of chloride and inhibit diffusion of oxide ions into the metal matrix because of the formation of protective layers.\(^\text{23,29}\) Furthermore, the predominant formation of \(\text{CoCl}_2\) occurs at a relatively high chlorine partial pressure \(p_{Cl_2} > 10^{-8}\) bar (Figure 14d) compared with the other alloying elements that were considered in this study. However, this protective effect of cobalt was not detected for the alloy HAYNES 188 \(w_{Co} = 35\%\) which showed the highest corrosion-induced mass loss among the tested alloys in this study. In contrast, Alloy 617 \(w_{Co} = 11\%\) showed the lowest mass loss among to the tested alloys with a similar chromium content \(w_{Cr} \approx 20\%\). According to Oryshch and Kostyrko, the addition of cobalt, molybdenum, and tungsten to a nickel–chromium matrix causes vacancies with a higher permeability of molten salt through protective nickel oxide scales. Once the molten chloride permeated through the oxide scale, it primarily forms liquid-phase metal chlorides that can dissolve in the molten salt.\(^\text{23}\) Based on thermodynamic calculations with FactSage SGPS database, cobalt chlorides as \(\text{CoCl}_2\) and \(\text{CoCl}_3\) are in liquid state at 1073 K with a vapor pressure below \(10^4\) Pa. On SEM/EDX images of HAYNES 188 and Alloy 617, this is indicated to cause localized pitting corrosion at the metal surface layer, and chromium depletion along the grain boundaries is significantly distinct on these alloys. This is consistent to a study of Cho et al. on nickel-cobalt-base alloys in LiCl–Li2O at 923 K that detects a more distinct intergranular attack, a higher mass loss, and higher quantities of dissolved alloying elements in the molten salt with increasing cobalt content of the alloy.\(^\text{31}\) Consequently, the ratio of cobalt and chromium content in an alloy is of high relevance for material mass loss and alloy matrix attack depth.

Overall, it can be stated that at 1073 K for low concentrations of oxygen \(p_{O_2} < 10^{-20}\) bar, the reaction of chromium oxide with the chloride melt is the dominant factor for the release of chlorine and the increase of the local chlorine partial pressure, respectively. This initiates a further attack of neighboring elements in the alloy matrix. Nickel and cobalt are calculated as most resistant against metal oxide formation \(p_{O_2} > 10^{-15}\) bar. However, cobalt and iron are considered to form liquid-phase metal chlorides when exposed to equivalent concentrations of chlorine and dissolve in the molten salt. Therefore, with a decreasing concentration of chromium and iron in an alloy, the formation of metal oxides and subsequent chlorine release occurs in lower quantities. Consequently, alloys with higher contents of nickel and molybdenum show an improved resistance to impurity-driven molten chloride corrosion, as detected in this study. The influence of impurities on the formation of cobalt, molybdenum, iron and nickel oxide and chlorine release needs to be further investigated to quantify the accelerating influence on molten chloride corrosion.

For technical applications, an oxygen partial pressure below \(p_{O_2} < 10^{-20}\) bar is difficult to achieve to completely inhibit corrosion reactions. Therefore, active corrosion control in molten KCl–LiCl (eut.) requires structural materials with a chromium content \(w_{Cr} < 8\%\) or advanced atmosphere control. Additional passive corrosion inhibition strategies as surface plating with nickel or molybdenum can potentially decrease structural material costs at equivalent corrosion resistance.

4. Conclusion

In this study, nine selected nickel-base alloys were exposed to molten KCl–LiCl (eut.) at 1073 K for 167 h under argon atmosphere to predict long-term corrosion behavior of structural materials for the application of molten chlorides in molten salt heat storage and heat transport facilities. HAYNES 242, Hastelloy B-3, and Hastelloy N showed no significant mass loss or even mass gain with minor corrosive attack on the alloy matrix, which can be contrasted to Alloy 600, Alloy 617, HAYNES 625, Hastelloy X, HAYNES 230, and HAYNES 188, which showed significant mass loss and were accompanied by severe chromium depletion. In accordance with studies on impurity-driven corrosion in molten salts, chromium appears to form chloride oxide with impurities as oxygen and water vapor at low oxygen partial pressures. This initiates further reactions that release \(\text{Cl}_2\) and further penetrates other alloying elements in the matrix such as Ni, Mo, Co, and Fe to form metal chlorides. A consistent protective oxide layer does not form. Instead, the reaction causes the depletion of chromium with the emergence of voids in the alloy matrix. Therefore, long-term corrosion resistance of structural materials in KCl–LiCl (eut.) at 1073 K can be achieved through the selection of alloys with a chromium content \(w_{Cr} < 8\%\) and by impurity control or the reduction of oxygen donors.

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**Conflict of Interest**
The authors declare no conflict of interest.

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concentrated solar power, heat-transfer fluids, high-temperature corrosion, molten chlorides, molten salts

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