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Formation of UO_2 on stainless steel 316 corroded in NaCl-KCl-UCl_x (x = 3,4) salts: Effect of crucible material

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<i>Keywords:</i> Molten chloride salt Uranium chloride Stainless steel 316 Corrosion Uranium dioxide Crucible	Stainless steel 316 was corroded in high temperature NaCl-KCl-UCl _x ($x = 3,4$) salts to investigate the effect of uranium-containing salts. The NaCl-KCl-UCl _x salts were prepared through the electrochemical oxidation of uranium rods. The ratio of UCl ₃ and UCl ₄ in the UCl _x salts was determined by X-ray absorption near-edge structure (XANES) analysis. The presence of UCl ₄ was further confirmed by the accelerated corrosion behaviors depending on the UCl _x concentration. After exposing stainless steel 316 to NaCl-KCl-UCl _x salts at 750 °C for 100 h using alumina, boron nitride, and glassy carbon crucibles, UO ₂ was formed on the surface in various forms, such as layers and/or particles. Additional corrosion experiments with NaCl-KCl-UCl _x -BaO salts were conducted to investigate the UO ₂ formation mechanisms. Results indicate that UO ₂ formation occurs via two pathways: reactions between salts and stainless steel 316 or deposition of UO ₂ formed in the salts. Regardless of how it forms, it is evident that UCl ₃ and UCl ₄ can produce UO ₂ through reactions with oxygen-related compounds (oxides, O ²⁻ , O ₂). The formation of UO ₂ can mitigate chromium depletion, but the precipitation of UO ₂ may lead to additional challenges. This study suggests the importance of both crucible selections for U-containing molten salt corrosion experiments and the consideration of UO ₂ formation in molten salt reactor environments.

1. Introduction

The necessity of nuclear energy has grown significantly to address the challenges of reducing carbon emissions and ensuring a stable energy supply. As the focus on nuclear energy continues to grow, interest in generation IV reactor systems is also rising. Among six selected generation IV reactor systems, the molten salt reactor (MSR) stands out for its distinctive advantages [1]. Molten salt reactors can operate at atmospheric pressure owing to the high melting points of molten salts, which minimizes mechanical stress on structural materials. Additionally, high boiling points of molten salts provide enough temperature margins between operation temperature and boiling points, which can enhance the safety of the nuclear power plant. The elevated operating temperatures of MSRs also contribute to higher thermal efficiency. Beyond these attributes, MSRs offer several other advantages, making them a promising technology for the next generation of nuclear reactors.

One of the critical challenges in the development of MSRs is the compatibility between salts and materials. Structural material corrosion intensively occurs due to high temperatures and the corrosive nature of the salts. Therefore, extensive research has been conducted to elucidate the corrosion mechanisms in molten salt environments and to identify corrosion-resistant materials [2–8]. It is widely recognized that the corrosion mechanism in molten salts involves the depletion of chromium (Cr), which has a relatively negative redox potential in molten salts. Conversely, materials with high concentrations of nickel (Ni) or molybdenum (Mo), which exhibit more positive redox potentials, demonstrate enhanced resistance to corrosion in molten salts.

Despite numerous corrosion studies conducted in molten salts, corrosion testing in fuel-containing salts remains crucial for the practical application of MSRs with liquid-state fuels. Uranium (U), a fuel material, exists in molten salts in either a trivalent or tetravalent state. In fluoride-based salts, the redox potentials of U(IV)/U(III) are lower than that of Cr, suggesting that both trivalent and tetravalent states of uranium fluoride are unlikely to influence material corrosion significantly [9]. In contrast, in chloride-based salts, the redox potentials of U(IV)/U(III) are higher than that of even Ni, indicating that the presence of UCl₄ accelerates corrosion. While corrosion of structural materials involving U-containing chloride salts has been sparsely investigated, these studies have been

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limited in scope, conducted with relatively low temperatures, short exposure durations, and limited analysis methods [10-13].

Therefore, in this study, the effects of U-containing chloride salts on material corrosion were investigated under various experimental conditions. Stainless steel 316 (SS 316), a potential structural material for MSRs, was selected for experiments. Uranium chloride with mixed valence states of U in a form of UCl_x was synthesized in NaCl-KCl through the electrochemical oxidation of U metal, and the valence state of U in the prepared salts was characterized using X-ray absorption near edge structure (XANES) spectroscopy. The mixed state of UCl₃ and UCl₄ was additionally confirmed with corrosion results with different concentrations of UCl_x. Corrosion experiments were performed in NaCl-KCl-UCl_x salts at 750 °C for 100 h using different types of crucibles. Notably, the formation of uranium dioxide (UO₂) was observed in specific cases. To elucidate the corrosion and UO₂ formation mechanisms, additional corrosion experiments were conducted with oxide-added systems.

2. Experimental methods

2.1. Materials

The chemical composition of SS 316 (Nilaco) used in this study, listed in Table 1, was analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES) and an elemental analyzer. SS 316 was cut to a size of 5 mm (W) \times 10 mm (H) \times 1.5 mm (T) for corrosion experiments. Specimens were abraded with 800 grit SiC paper and cleaned with ethanol.

High-purity NaCl (99.99 %, Thermo Fisher Scientific, ultra-dry, <100 ppm residual water) and KCl (99.998 %, Thermo Fisher Scientific, ultra-dry, <100 ppm residual water) were used as base salts for the experiments. NaCl and KCl were mixed in a molar ratio of 50.6:49.4. Barium oxide (BaO, 99.99 %, Sigma-Aldrich) was introduced as the oxide material. U rods (NBS-SRM 960) were utilized to prepare NaCl-KCl-UCl_x salts.

2.2. Electrochemical and corrosion experiments

All experiments were conducted in a glovebox filled with Ar (99.999%). O_2 and H_2O concentrations in the glovebox were controlled below 2 ppm. The temperature conditions were adjusted with the electrical furnace attached under the glovebox.

Electrochemical experiments were conducted to prepare NaCl-KCl-UCl_x salts. A potentiostat (SP-240, BioLogic) and a three-electrode system were introduced. U rod, tungsten (W) rod, and platinum (Pt) rod were utilized as working electrode, counter electrode, and reference electrode, respectively. The NaCl-KCl mixture was melted at 700°C in a glassy carbon crucible. All electrodes were inserted into the completely melted salts. Following the oxidation of U, the prepared NaCl-KCl-UCl_x salts were sampled using quartz tubes.

Corrosion experiments were conducted using three different types of crucibles with 10 mm inner diameter: Al_2O_3 (alumina), BN (boron nitride), and glassy carbon. 4 g of salts and an SS 316 specimen were placed in each crucible at room temperature. The position of the SS 316 specimen was carefully controlled so as not to touch the crucibles. The crucibles were then covered with lids and placed in a stainless steel 304 cell. The temperature was increased at a rate of 2.5 °C/min. After maintaining 750 °C for 100 h, the furnace was cooled down to room temperature. The salts were dissolved with deionized water to retrieve the specimens.

Table 1

Chemical com	position of	SS	316	(wt%).
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Alloy	Fe	Cr	Ni	Мо	Si	Mn	С
SS 316	bal.	16.40	9.95	1.94	0.72	0.96	0.05

2.3. Characterization

The XANES measurements were performed using a laboratory-based X-ray absorption spectroscopy system (hiXAS, HP Spectroscopy) to characterize the valence states of UCl_x prepared through electrochemical oxidation of U metal [14,15]. The X-ray energy was calibrated using a Zr metal foil. Quenched NaCl-KCl-UCl_x samples were pelletized to a thickness of 1 mm inside a glovebox and placed in a custom-made sealing holder composed of Al metal and Kapton tape. Blank measurements without salts were conducted first, followed by measurements of the NaCl-KCl-UCl_x samples. The XANES analysis was performed using the Demeter software package [16].

The weight of specimens was measured using an electronic balance (Mettler Toledo, XSR105DUV) with a resolution of 0.01 mg before and after the corrosion experiments. Corrosion behaviors were investigated with several analytical instruments placed in KAIST analysis center for research advancement (KARA). Microstructure changes along the surface and cross-section were analyzed with scanning electron microscope (SEM, SU5000, Hitachi) and field emission scanning transmission electron microscopy (FE-STEM, Talos F200X, Thermo Fisher) equipped with energy-dispersive X-ray spectroscopy (EDS). Samples for STEM analysis were prepared by the focused ion beam (FIB, Helios Nanolab 450 F1, FEI company). Characterization of corrosion products was conducted with grazing incidence X-ray diffraction (GIXRD, Ultima IV, RIGAKU, 40 kV, 40 mA, incident angle of 2°, 5°/min) and X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific).

3. Results

3.1. Preparation and characterization of NaCl-KCl-UCl_x

The electrochemical oxidation of U metal was performed via chronopotentiometry in NaCl-KCl molten salts at 700 °C. A constant current of 20 mA was applied to U rods for 3 h and 30 min to oxidize U metal to U chlorides. In molten chloride salts, U chlorides are stable in two valence states: trivalent and tetravalent. Therefore, prepared NaCl-KCl-UCl_x salts were expected to have a mixed valence state of U ions.

To determine the valence state distribution, XANES spectroscopy was conducted. Fig. 1 shows the XANES spectrum of the NaCl-KCl-UCl_x sample. The L_{III} edge of uranium was observed at 17170.3 eV. The U L_{III} edge for UCl₃ mixed with boron nitride has been reported at 17169 eV, while UCl₄ melted in LiCl-KCl has been observed at 17172.3 eV [17]. This implies that the sample contains both trivalent and tetravalent states of U. Based on the simplified assumption that the edge energy is linearly proportional to the ratio of UCl₃ and UCl₄, the proportions of



Fig. 1. U L_{III} edge XANES spectrum of NaCl-KCl-UCl_x.

 $\rm UCl_3$ and $\rm UCl_4$ in the prepared NaCl-KCl-UCl_x were roughly estimated to be around 60 % and 40 %, respectively.

The concentration of UCl_x in the prepared NaCl-KCl salt was determined by ICP-OES to be 0.44 wt%, based on the weight of uranium chlorides. This result was significantly lower than the target concentration of 2 wt% UCl₃ in NaCl-KCl, based on the charge calculation, 252 coulombs in 15 g NaCl-KCl. The low oxidation efficiency was attributed to the counter-electrode reaction, involving the cation reduction, either through the direct electrochemical reduction of UCl_x or the chemical reduction of UCl_x by reduced Na or K. For corrosion experiments, prepared NaCl-KCl-UCl_x salts were diluted to 0.1 wt% UCl_x or 0.2 wt% UCl_x.

3.2. Corrosion with different concentration of UCl_x

The presence of UCl₄ in the prepared UCl_x was further supported by corrosion experiments conducted at varying concentrations of UCl_x. SS 316 specimens were exposed to molten salts in glassy carbon crucibles at 750 °C for 100 h. The experiments utilized two different concentrations of salts: NaCl-KCl-UCl_x (0.1 wt%) and NaCl-KCl-UCl_x (0.2 wt%).

Table 2 represents the weight change of SS 316 after the corrosion tests. The results indicate that the weight loss increases with higher UCl_x concentrations. Additionally, cross-sectional analyses were performed using SEM-EDS mapping, as shown in Fig. 2. The analyses revealed that both the depth of cross-sectional corrosion attack and the extent of Cr dissolution increased with higher UCl_x concentrations. The weight change data and cross-sectional observations confirmed that the corrosion reaction intensifies with higher UCl_x concentration. These findings strongly suggest that UCl_x contains corrosion-accelerating compounds, most likely UCl_4 .

3.3. Corrosion with different crucibles

Three different crucibles, alumina, boron nitride, and glassy carbon, were utilized to conduct corrosion experiments of SS 316 in prepared NaCl-KCl-UCl_x at 750 °C for 100 h to investigate the corrosion behaviors with various experimental conditions. The concentration of UCl_x was diluted to 0.1 wt%. Table 3 presents the results of weight change. SS 316 corroded in the glassy carbon crucible exhibited the highest weight loss. In contrast, SS 316 corroded in alumina and boron nitride crucibles showed a relatively lower weight loss, even under the extreme corrosion conditions of 750 °C

The corrosion products formed on the SS 316 surface were analyzed using GIXRD, and the results are shown in Fig. 3. UO_2 was detected on the SS 316 surfaces when alumina and boron nitride crucibles were used for corrosion experiments. The formation of UO_2 , originating from the salt rather than the SS 316, contributed to the smaller weight loss. In contrast, only metal carbides were observed on the SS 316 corroded in the glassy carbon crucible. Cr depletion results in the formation of carbides composed of Ni and Mo.

In addition, the XRD results revealed peaks corresponding to the BCC phase in all specimens. While these peaks may indicate the presence of ferrite or martensite, both phases are generally unstable at elevated temperatures, making their presence after exposure to 750 °C salts unlikely. However, several studies have reported the formation of ferrite/martensite phases following high-temperature corrosion experiments [6,18,19]. It is known that Cr depletion in the austenite phase can lead to a transformation into the martensite phase [20]. Further investigation is

Table 2

Weight changes of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) and NaCl-KCl-UCl_x (0.2 wt%) at 750 °C for 100 hrs with glassy carbon crucible.

Conditions	Weight change [mg/cm ²]
NaCl-KCl-UCl _x (0.1 wt%)	-1.79
NaCl-KCl-UCl _x (0.2 wt%)	-2.36

required to conclusively identify the phase; however, the martensite phase likely formed in the Cr-depleted region during the slow cooling following the corrosion experiments [18].

These findings, different corrosion products depending on crucibles, indicate that crucible materials are involved in the corrosion reactions. UO_2 was formed for the case using alumina and boron nitride crucibles. The common thing for two crucibles is that oxides are present. Alumina crucibles are oxides themselves, and boron nitride crucibles are known to contain some B_2O_3 impurities. For this reason, it is assumed that the UO_2 formation was related to the presence of oxides.

The surface of corroded SS 316 was characterized via SEM with backscattered electron (BSE) and EDS. Fig. 4(a) represents the surface of SS 316 corroded in the alumina crucible. The surface is uniformly covered with particles, along with some larger particles. The bright contrast of these particles in BSE images indicates that particles are composed of heavy elements. EDS analysis revealed that these particles are rich in U and oxygen (O). Similar U- and O-rich particles were observed in Fig. 4(b), which shows the surface of SS 316 corroded in the boron nitride crucible. However, in this case, the particles were not evenly distributed, and only large particles were sparsely present.

Fig. 4(c) representing the surface of the specimen corroded in the glassy carbon crucible shows totally different states. The bright particles in the BSE image were identified as Ni- and Mo-rich carbides based on EDS analysis and the XRD results shown in Fig. 3. U- and O-rich particles were not able to be found on the surface. Furthermore, a significant dissolution along the grain boundaries was observed.

The surface states align with the weight change results. The SS 316 corroded in the alumina crucible exhibited the lowest weight loss, attributed to the homogeneous formation of UO_2 on the surface. In contrast, the SS 316 corroded in the glassy carbon crucible showed the highest weight loss, due to the absence of UO_2 and the dissolution along the grain boundary.

Cross-sectional corrosion behaviors were analyzed by SEM and STEM. Fig. 5(a) shows SEM-EDS mapping results of the sample corroded in the alumina crucible. U and O were enriched on the surface, forming a layered structure. Additionally, some U- and O-rich particles were observed. The Cr depletion was also observed near the surface. Fig. 5(b) represents the cross-sectional image of SS 316 corroded in the boron nitride crucible. In this case, U and O existed as particles rather than layers, and the depth of Cr depletion was increased. When the glassy carbon crucible was used in corrosion experiments, regions enriched with U and O were difficult to find, as shown in Fig. 5(c). Instead, an intensive grain boundary corrosion occurred, with a Cr depletion depth of more than 10 μ m. UO₂, which has a lower Gibbs free energy of formation than other metal oxides, appears to act as a barrier layer against Cr depletion [21].

Fig. 6(a), 6(b), and 6(c) show the results of STEM-EDS mapping for samples corroded in alumina, boron nitride, and glassy carbon crucibles, respectively. Using the alumina crucible, U- and O-rich layers with thicknesses from 10 nm to 50 nm were clearly observed. These layers appeared to be homogeneously distributed on the surface. In contrast, in the other two cases, there were no enriched U and O regions even at the nanometer scale.

Further analysis using XPS was conducted to provide a detailed analysis of the corrosion products formed on the surface. XPS spectra of U shown in Fig. 7 were obtained after 60 s of Ar-ion sputtering to eliminate the surface contamination. U $4f_{7/2}$ and U $4f_{5/2}$ peaks were observed near 380.2 eV and 391.1 eV, close to U(IV) states, for specimens corroded in alumina, boron nitride, and glassy carbon crucibles [22]. These U(IV) peaks are attributed to UO₂, as previously confirmed by the GIXRD analysis of SS 316 corroded in alumina and boron nitride crucibles. The noteworthy observation is that SS 316 samples corroded in the glassy carbon crucible, which did not exhibit U- and O-rich regions in SEM and STEM analyses, showed the U(IV) state on the surface in the XPS spectra. This suggests that UO₂ is also present on the surface of the samples corroded in the glassy carbon crucible. Slight amounts of



Fig. 2. Cross-sectional SEM and EDS mapping images of SS 316 corroded at 750 °C for 100 h with glassy carbon crucible in (a) NaCl-KCl-UCl_x (0.1 wt%), (b) NaCl-KCl-UCl_x (0.2 wt%).

Table 3

Weight changes of SS 316 corroded in NaCl-KCl-UCl _x (0.1 wt%) at
750 °C for 100 h with different crucibles.

Used crucibles	Weight change [mg/cm ²]
Alumina	-0.23
Boron nitride	-0.46
Glassy carbon	-1.79



Fig. 3. GIXRD of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) at 750 $^\circ C$ for 100 h with different crucibles.

oxygen (O_2) gas in the atmosphere or oxide impurities in the salts are expected to contribute to the UO_2 formation in the glassy carbon crucible. However, its visualization using SEM or STEM analyses was challenging due to the very tiny quantities.

3.4. Corrosion with oxide impurities

Previous results indicate that UO_2 can be formed under specific conditions, such as reactions with oxides or oxygen gas. Another possible reaction that has to be considered is the reaction with free oxygen ions (O²), which may be generated through the dissolution of oxides irrespective of the solubility in molten salts. To further investigate the mechanism of UO_2 formation, O^{2-} was intentionally introduced with BaO. BaO was selected because Ba cations, Ba^{2+} , are not expected

to affect corrosion reaction due to the more negative redox potential compared to alloying elements of SS 316 [23]. The solubility of BaO in NaCl-KCl at 700 °C was reported as 0.06 wt%, so the added amount of BaO was controlled to be 0.04 wt% to supply only O^{2-} , not other compounds [24].

Fig. 8 presents the surface SEM and BSE images of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%)-BaO (0.04 wt%) using the glassy carbon crucible at 750 °C for 100 h. Similar surface corrosion features were observed when compared to SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) under the same conditions. Dissolution along the grain boundaries was evident, and Ni- and Mo-rich carbides were detected. A notable difference, however, was the presence of U- and O-rich particles on the surface, which appeared as bright particles in the BSE images. These particles were distributed across the entire surface.

GIXRD was performed to characterize corrosion products formed on the surface, and the results are shown in Fig. 9. Ni- and Mo-rich carbides were detected in consistency with observations of SS 316 corroded under the same conditions without BaO. A key difference in comparison to the specimen corroded without BaO is the detection of UO₂, which is identified as U- and O-rich particles confirmed in Fig. 8. Therefore, it can be concluded that O^{2-} may also contribute to the formation of UO₂ in molten NaCl-KCl-UCl_x systems.

4. Discussion

4.1. Formation of UO_2 from the reaction between salts and SS 316

To summarize the analyzed results, due to the presence of oxides, O_2 gas, and O^{2° , UO_2 was formed on the SS 316 surface in NaCl-KCl-UCl_x. UO_2 can appear via two pathways: direct formation from reactions between salts and SS 316 or deposition of UO_2 formed in salts.

 UO_2 can remain stable on the SS 316 surface if it forms through reactions involving SS 316. One likely mechanism is the reaction between U-containing salts and Cr_2O_3 , which develops from Cr of SS 316. Cr_2O_3 can form in molten salts due to impurities such as O^2 -, HCl, and Cl₂, originating from trace amounts of H₂O and O₂ in the cover gas, as described in Eqs. (1) and (2).

$$H_2O(g) + 2CI'(l) \leftrightarrow O^{2'}(l) + 2HCl(g)$$
(1)

$$O_2(g) + 4Cl^{-}(l) \leftrightarrow 2O^{2-}(l) + 2Cl_2(g)$$

$$(2)$$

These impurities react with Cr in SS 316, leading to Cr_2O_3 formation through the following mechanisms, represented in Eqs. (3) and (4).

$$2Cr(s) + 3O^{2}(l) + 6HCl(g) \leftrightarrow Cr_{2}O_{3}(s) + 6Cl(l) + 3H_{2}(g)$$
(3)



Fig. 4. Surface SEM and BSE images of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) at 750 $^{\circ}$ C for 100 h with (a) alumina crucible, (b) boron nitride crucible, (c) glassy carbon crucible.

 $2Cr(s) + 3O^{2-}(l) + 3Cl_2(g) \leftrightarrow Cr_2O_3(s) + 6Cl^{-}(l)$ (4)

Eqs. 3 and 4 suggest that higher O^{2-} concentrations in the salts enhance Cr_2O_3 formation. As shown in Fig. S1(a) and Table S1 of the supplementary materials, Cr-rich oxides were extensively formed when the alumina crucible was used for the corrosion experiments of SS 316 in NaCl-KCl, without UCl_x. Similar oxides appeared with the boron nitride crucible but not with the glassy carbon crucible, as can be seen in Fig. S1 (b), Fig. S1(c), and Table S1. This suggests that the dissolution of the alumina crucible itself or the dissolution of B₂O₃ impurities in the boron nitride crucible provides additional O²⁻ into salts, promoting increased Cr₂O₃ formation. In addition, the surface analysis results of SS 316 corroded in NaCl-KCl-BaO (0.04 wt%) salts demonstrated the Cr-rich oxide formation from the presence of O²⁻ ions, as illustrated in Fig. S2 and Table S2.

Formed Cr_2O_3 can react with both UCl₃ and UCl₄, leading to the formation of UO₂, as shown in Eqs. (5) and (6).

$$\begin{aligned} & \text{UCl}_4(l) + 2/3\text{Cr}_2\text{O}_3(s) \leftrightarrow \text{UO}_2(s) + 4/3\text{CrCl}_3(l) \end{aligned} \tag{5} \\ & (\Delta \text{G} = -12.13 \text{ kJ/mol at 750 °C}) \\ & \text{UCl}_3(s) + 2/3\text{Cr}_2\text{O}_3(s) \leftrightarrow \text{UO}_2(s) + 4/3\text{CrCl}_3(l) + 1/6\text{Cl}_2(g) \end{aligned} \tag{6}$$

($\Delta G = -31.55 \text{ kJ/mol}$ at 750 °C)

The HSC Chemistry 10 was used to calculate the Gibbs free energy of the reactions [25]. Some limitations may exist, as it is challenging to accurately simulate the molten state of salts. Despite these limitations, both experimental and calculation results clearly demonstrate that UO_2 can be formed on the SS 316 surface through salt- Cr_2O_3 reactions.

4.2. Deposition of UO_2 formed in salts

Another possible pathway for UO₂ formation on the SS 316 surface is the deposition of UO₂ formed in the salts. Although it may attach to the surface unstably, it can still contribute to UO₂ presence on SS 316. The first mechanism for UO₂ formation in the salt is the reaction between KCl-UCl₄ and the alumina crucible, as represented in Eq. (7).

$$4\text{KCl}(s) + 2/3\text{Al}_2\text{O}_3(s) + \text{UCl}_4(l) \leftrightarrow 4/3\text{K}_3\text{AlCl}_6(s) + \text{UO}_2(s) \tag{7}$$

$$(\Delta G = -8.74 \text{ kJ/mol at } 750 \degree \text{C})$$

The second possible reaction that could lead to the UO_2 formation involves reactions between salts and O^{2^2} . Considering that the valence state of uranium in UCl_4 is tetravalent, such compounds with the same



Fig. 5. Cross-sectional SEM and EDS mapping images of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) at 750 °C for 100 h with (a) alumina crucible, (b) boron nitride crucible, (c) glassy carbon crucible.

valence state are likely to react with O^{2-} to form UO_2 , as described in Eq. (8).

$$UCl_4(l) + 2O^{2-}(l) \leftrightarrow UO_2(s) + 4Cl^{-}(l)$$
(8)

Among the oxides that can form under the experimental conditions, UO_2 is the most thermodynamically stable, as indicated in Table 4. Consequently, the reaction described by Eq. (8) is likely to occur if O^{2-} ions are present in the salts. These O^{2-} ions may originate from impurities in the salts themselves, the dissolution of oxides on the SS 316 surface, and/or the dissolution of crucible materials used in the experiments.

The third possible mechanisms for the UO_2 formation are chemical reactions with O_2 gas impurities. Although all experiments were conducted in the Ar-filled glovebox, it is virtually impossible to completely eliminate trace amounts of O_2 gas. O_2 gas can react with both UCl₃ and UCl₄ to form UO₂ based on the mechanisms described in Eq. (9) and Eq 10.

$$O_2(g) + UCl_3(s) \leftrightarrow UO_2(s) + 3/2Cl_2(g) \tag{9}$$

 $(\Delta G = -260.34 \text{ kJ/mol at } 750 \degree \text{C})$

$$O_2(g) + UCl_4(l) \leftrightarrow UO_2(s) + 2Cl_2(g)$$
(10)

$$(\Delta G = -173.02 \text{ kJ/mol at } 750 \degree \text{C})$$

Although these calculations cannot perfectly reflect the molten state, these reactions likely contributed to UO_2 formation when the glassy carbon crucible was used. However, due to the very low concentration of O_2 gas in the glovebox atmosphere, only trace amounts of UO_2 were formed.

4.3. UO_2 formation in perspectives of molten salt corrosion experiments and MSR environments

The described mechanisms suggest that most UO_2 can be formed from UCl_3 and UCl_4 in the presence of oxygen-related compounds (oxides, O^{2^2} , O_2). This means that crucibles containing oxides are inappropriate to use for U-containing molten salt corrosion experiments. Oxide-rich conditions, which are far from the MSR environments, can mislead the interpretation of corrosion results.

From the view of practical applications in MSRs, fuel salts need to primarily contain UCl₃ due to the corrosive nature of UCl₄ in chloridebased salts. Therefore, UO₂ can be formed in MSR from the dominant UCl₃ of fuel salts if oxygen-related impurities are introduced. Another source, UCl₄, is expected to form UO₂ even more easily due to the same valence state of U. UCl₄ can be generated in MSR environments if oxidative conditions are formed in MSRs, as observed in the molten salt reactor experiment (MSRE) conducted at Oak Ridge National Laboratory in the 1960s [26]. Oxidative conditions in MSRs can arise not only due to unintended impurities but also as a result of fission processes. Fission products in molten salts can exist in multiple valence states, leading to oxidation reactions of fuel salts or structural materials to maintain electroneutrality. Since the redox conditions of chloride-based MSRs formed by nuclear fission have been expected to be oxidative, UCl₄ can be generated under these conditions [27,28].

Homogeneous UO_2 formation could serve as a mitigation strategy to reduce Cr dissolution along the grain boundary in molten salts, as observed in Fig. 5. However, the impact of UO_2 precipitation on the structural materials must be carefully evaluated, as fission reactions may occur at the UO_2 precipitate and alter the concentration of liquid fuels.

5. Conclusion

In this study, corrosion behaviors of SS 316 in NaCl-KCl-UCl_x salts at 750 °C for 100 h were investigated. The NaCl-KCl-UCl_x salts were prepared by the electrochemical oxidation of the U rod. XANES spectroscopy confirmed the presence of both UCl₃ and UCl₄ in the prepared NaCl-KCl-UCl_x salts. The enhanced corrosion of SS 316 in NaCl-KCl-UCl_x (0.2 wt%) salts compared to NaCl-KCl-UCl_x (0.1 wt%) salts further demonstrated the presence of UCl₄ in the UCl_x salts.

Corrosion experiments of SS316 were performed in NaCl-KCl-UCl_x (0.1 wt%) salts under various experimental conditions, including different crucible materials (alumina, boron nitride, glassy carbon) and the presence of oxide impurities. With the alumina crucible, UO_2 formed



Fig. 6. Cross-sectional STEM-EDS mapping images of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) at 750 °C for 100 h with (a) alumina crucible, (b) boron nitride crucible, (c) glassy carbon crucible.



Fig. 7. XPS of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) at 750 $^\circ C$ for 100 h with different crucibles.

as layers on the SS 316 surface, whereas in the boron nitride crucible, UO_2 appeared as particles. In experiments with the glass carbon crucible, the detection of UO_2 was challenging using SEM or STEM analysis; however, XPS results provided evidence of its presence. When the corrosion experiment was conducted with NaCl-KCl-UCl_x (0.1 wt %)-BaO salts using the glassy carbon crucible, UO_2 particles were clearly observed on the surface of SS 316.

The experimental results indicate that oxygen-containing compounds can readily produce UO_2 through reactions with UCl_3 and UCl_4 . This highlights the importance of careful material selection in corrosion experiments involving U-containing molten salts. Additionally, the potential effects of UO_2 on structural materials should be considered in the development of MSR technology.

CRediT authorship contribution statement

Yun Jong-II: Writing – review & editing, Supervision, Funding acquisition, Conceptualization. Jang Changheui: Writing – review & editing, Methodology, Funding acquisition, Conceptualization. Kim Sumin: Methodology, Conceptualization. Eom Hyun Joon: Methodology, Conceptualization. Yoon Seokjoo: Writing – review & editing, Investigation, Formal analysis. Park Jun Woo: Writing – original draft,



Fig. 8. Surface (a) SEM and (b) BSE images of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%)-BaO (0.04 wt%) at 750 °C for 100 h with glassy carbon crucible.



Fig. 9. GIXRD of SS 316 corroded in NaCl-KCl-UCl_x (0.1 wt%) and NaCl-KCl-UCl_x (0.1 wt%)-BaO (0.04 wt%) at 750 $^\circ\text{C}$ for 100 h with glassy carbon crucible.

Table 4

Gibbs free energy of formation for oxides that can be formed in experimental systems at $750 \degree C$ (HSC Chemistry 10) [25].

Sibbs free energy of formation (kJ/mole $\rm O_2$), at 50 $^\circ\rm C$
-440.10
-549.22
-580.04
-677.03
-902.53
-908.43

Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT in order to improve readability and language of the manuscript. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.corsci.2025.112979.

Data availability

Data will be made available on request.

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