Effect of Crucible Material on Corrosion of 316 Stainless Steel in Uranium-Containing Molten Chloride Salts

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1. Introduction

Molten salt reactors (MSRs) utilize fuel-containing salts in the primary loop. In molten chloride salt reactors, which are advantageous for fast-spectrum operation [1], uranium trichloride (UCl_3) serves as the fuel. Since UCl_3 is in direct contact with structural materials in the primary system, its effect on material corrosion must be evaluated to ensure the long-term safety of the reactor.

Previous research on molten fluoride salt reactors, widely studied in the 1950s and 1960s, found that uranium tetrafluoride (UF_4) induced selective chromium (Cr) depletion from alloys. This phenomenon occurred because the redox potential of the U(IV)/U(III) couple is similar to that of the Cr(II)/Cr(0) couple [2]. In chloride salts, significant corrosion is not expected if the fuel is mainly composed of UCl_3, due to the low redox potential of the U(III)/U(0) couple.

However, unintended reactions can introduce additional corrosion pathways. For instance, impurities may oxidize UCl_3 to corrosive uranium tetrachloride (UCl_4), or UCl_3 could react with oxide layers on the material surfaces. These secondary reactions could threaten the stability of reactors. Therefore, fundamental corrosion experiments using UCl_3 are essential for understanding the corrosion behavior of structural materials in molten chloride salt reactors.

In this study, corrosion experiments were conducted for 100 hours at 750°C in molten NaCl-KCl-UCl_x (x=3, 4) salts, which were prepared in the laboratory. 316 stainless steel (316 SS) was selected as the test alloy. To investigate the influence of container materials, various crucibles were utilized for the experiments. The authors have previously discussed how crucible materials affect corrosion behavior [3]. This study introduced an additional system with a different UCl_3/UCl_4 ratio to demonstrate the corrosion mechanisms.

2. Experimental

2.1. Setup

All experiments were conducted inside the glovebox filled with high-purity (99.999%) argon (Ar) gas. The temperature was controlled using an electrical furnace positioned beneath the glovebox.

The experiments utilized lidded crucibles made of alumina and glass carbon with an inner diameter of 10 mm. 316 SS specimens with dimensions of 5mm × 10mm × 1.5mm were ground with 2,000 grit sandpaper and suspended by 316 SS wires to be fully submerged in the molten salts. The base salt was prepared by mixing equimolar amounts of NaCl (99.99%, Thermo Fisher Scientific) and KCl (99.99%, Thermo Fisher Scientific).

2.2. Preparation of Uranium-containing Chloride Salts

NaCl-KCl-UCl_x (x=3, 4) salts were prepared by the electrochemical oxidation of uranium (U) metal inside NaCl-KCl molten salts. U metal was set as a working electrode, and 20mA of oxidation currents were applied for 3 hours and 30 minutes. As both U(III) and U(IV) can be produced from the oxidation, the reduction of UCl_4 to UCl_3 was further carried out via U comproportionation reaction by U metal insertion, as shown in Eq. (1).

$$U + 3UCl_4 \leftrightarrow 4UCl_3 \tag{1}$$

This study compares two salt samples. U-1, which used in the previous study [3], was prepared without reducing U. In contrast, U-2 was newly prepared for this work by applying the U comproportionation reaction for 17 hours after electrochemical oxidation. Both salts, composed of UCl_x mixed with NaCl-KCl, were sampled using quartz tubes and subsequently diluted with NaCl-KCl to 0.1 wt% UCl_x for the corrosion experiments.

To determine the valence state distribution, XANES (X-ray absorption near edge structure) spectroscopy was conducted. Figure 1 shows the XANES spectrum of U-1 and U-2 samples. The L_{III} edges of U-1 and U-2 were observed at 17170.3 eV and 17169.2 eV, respectively. The U L_{III} edge for UCl_3 has been reported at 17169 eV, while UCl_4 has been observed at 17172.3 eV [4]. Therefore, it was confirmed that the U-2 sample consisted predominantly of UCl_3, while the U-1 sample contained a significant amount of UCl_4.

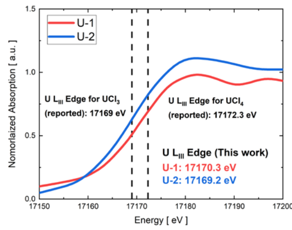

Figure 1. U L_{III} edge XANES spectrum of NaCl-KCl-UCl_x (U-1 and U-2)

2.3. Characterization

Characterization of corrosion products was conducted with grazing incidence X-ray diffraction (GIXRD, Ultima IV, RIGAKU, 40kV, 40mA, incident angle of 2°, 5°/min) and X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific). Microstructure changes along the surface and cross-section were analyzed with a scanning electron microscope (SEM, SU5000, Hitachi) equipped with energy-dispersive X-ray spectroscopy (EDS) and back-scattered electron (BSE) detector.

3. Results and Discussion

GIXRD was used to identify the corrosion products on 316 SS specimens after 100 hours of corrosion at 750°C. Figure 2(a), which was also presented in the previous study [3], shows the results for specimens corroded in the U-1 salt using different crucibles. In comparison, Figure 2(b) shows the results for specimens corroded in the newly prepared U-2 salt under the same conditions. The detection of XRD peaks for uranium dioxide (UO_2) was determined by the crucible material, independent of the UCl_3/UCl_4 ratio. UO_2 peaks were consistently detected in experiments using the alumina crucible but were absent in those using the glassy carbon crucible.

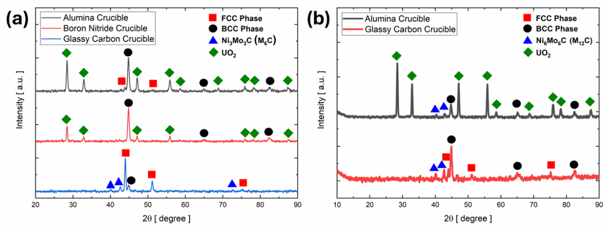

Figure 2. GIXRD of 316 SS corroded with different crucibles (a) in NaCl-KCl-UCl_x (U-1, 0.1wt%), (b) in NaCl-KCl-UCl_x (U-2, 0.1wt%),

For the experiments using U-1 salt, XPS analysis confirmed the presence of UO_2 on the 316 SS sample corroded in the glassy carbon crucible. As shown in Figure 3 (reproduced from the previous study [3]), U(IV) peaks, attributed to UO_2, were detected on specimens from all three crucible types: alumina, boron nitride, and glassy carbon. This confirms that UO_2 formed on the 316 SS surface corroded in the glassy carbon crucible, even though it was not detected by GIXRD.

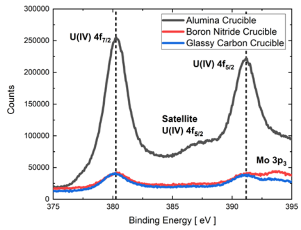

Figure 3. XPS of 316 SS corroded with different crucibles in NaCl-KCl-UCl_x (U-1, 0.1wt%)

The 316 SS sample, corroded in a glassy carbon crucible containing U-2 salts, was further analyzed by SEM and BSE. The resulting images, presented in Figure 4, show distinct regions that appear as bright white particles in the BSE image. EDS of these regions revealed high concentrations of both U and oxygen (O) (U ≈ 20 wt%, O ≈ 15 wt%). Although the inherent uncertainty of SEM-EDS analysis makes it difficult to ascertain the exact compound, these high U and O concentrations strongly suggest the formation of UO_2.

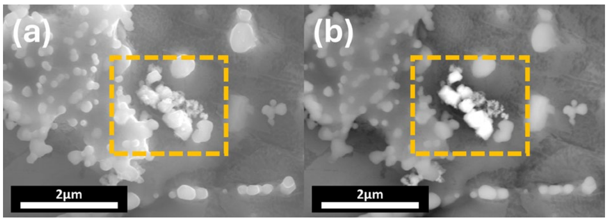

Figure 4. (a) SEM and (b) BSE images of 316 SS corroded in NaCl-KCl-UCl_x (U-2, 0.1wt%) with glassy carbon crucible

In conclusion, UO_2 can be formed on the 316 SS surface regardless of the initial UCl_3/UCl_4 ratio. The formation mechanism can be attributed to reactions between UCl_x and metal oxides. For instance, Cr_2O_3 can be formed on 316 SS surfaces during corrosion in NaCl-KCl molten salts. The potential chemical reactions between UCl_x and Cr_2O_3 are described in Eq. (2) and Eq. (3).

$$UCl_4(l) + 2/3Cr_2O_3(s) \leftrightarrow UO_2(s) + 4/3CrCl_3(s) \quad (2)$$

$$UCl_3(s) + 2/3Cr_2O_3(s) \leftrightarrow UO_2(s) + 4/3CrCl_2(s) + 1/6Cl_2(g) \quad (3)$$

When using alumina crucibles, oxides from the crucible material can dissolve into the molten salt. This process enhances the formation of Cr_2O_3, which in turn increases the amount of UO_2 produced. In contrast, with glassy carbon crucibles, the only significant source of oxygen is the trace amount of O_2 present in the high-purity argon atmosphere. Consequently, the quantity of UO_2 formed under these conditions is substantially lower.

4. Conclusion

This study investigated the corrosion behaviors of 316 SS in NaCl-KCl-UCl_x (x=3,4) molten salts using different crucible materials: alumina and glassy carbon. NaCl-KCl-UCl_x salts were prepared via the electrochemical oxidation of U metal, followed by U comproportionation reaction. Analysis of the corroded samples revealed UO_2 as a primary corrosion product. A key finding was that the amount of UO_2 produced varied depending on the crucible material used. These results highlight the critical importance of selecting crucible materials for corrosion experiments involving U salts to avoid the misinterpretation of experimental outcomes.

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