

## Various methodologies to mitigate structural material corrosion in molten NaCl–MgCl<sub>2</sub> system

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### 1. Introduction

Molten salt reactor (MSR) is one of the GEN-IV reactors which uses molten salt as its fuel and primary coolant. Compared the conventional nuclear power reactors these days, MSR has various advantages such as high thermal and economic efficiency, safety, availability of miniaturization, and in particular, transuranic (TRU) element combustion is available and on-power refueling system that can guarantee the continuous operation. Due to these advantages, various countries and research institutes are actively researching the MSR. However, the biggest stumbling block of the MSR is the corrosion of its structural materials due to highly corrosive molten salt. [1, 2]

The major causes of molten salt corrosion can be summarized as follows; electrochemical and chemical reactions due to the fissile element, fission products, and water–oxygen impurities. [3] Various techniques to mitigate molten salt corrosion were investigated, [4, 5] but, most of the strategies are based on a fluoride system. The chloride system has many similarities to the fluoride system, but their physical and chemical properties are not exactly the same. Therefore, it is necessary to confirm whether the techniques to mitigate molten salt corrosion which was developed based on the fluoride system are applicable to the chloride system.

In this study, various techniques to reduce molten salt corrosion were examined. Residual moisture and oxygen which are regarded as the most deleterious impurities were eliminated chemically and electrochemically. Corrosion behavior change due to introduced metallic elements such as Mg, Nb, Mo, and W were analyzed, and the sacrificial metal effect was confirmed. Redox potential control to reduce corrosion was also studied by adjusting the  $\text{Eu}^{3+}/\text{Eu}^{2+}$  ratio. Microstructural change of the Ni-based alloy was analyzed by SEM–EDS and salt content was analyzed by ICP–OES and element analyzer.

### 2. Experimental Setup

#### 2.1. Experimental equipment

It is well known that some elements in the structural materials can accelerate or decelerate the molten salt-induced corrosion. However, the purpose of this study is to develop the methodologies to mitigate molten salt corrosion, and 80Ni–20Cr alloy without any other alloying elements was selected as the target structural

material. The alloy was generated by casting and hot-rolling with heat treatment and the specimen was cut by waterjet and polished using 400-grit sandpaper and finished using a 1-micrometer diamond suspension.

All electrochemical experiments and specimen–reagent preparation were conducted in a glovebox filled with Ar (99.996%). NaCl (Alfa Aesar, 99.99%) and MgCl<sub>2</sub> (Alfa Aesar, 99.99%) were preheated at 200 °C, 400 °C, and 600 °C sequentially for 24 hours each to remove any residual moisture and oxygen. The eutectic composition of the salt, 58.0 at.% NaCl–42.0 at.% MgCl<sub>2</sub>, was used due to its relatively low melting point of approximately 459 °C, and its composition was confirmed by ICP–OES (700-ES, Varian). Prepared NaCl–MgCl<sub>2</sub> salt was also analyzed by element analyzer (Flash 2000, Thermo) and it was confirmed that a small amount of moisture and oxygen were still remaining in the salt.

#### 2.2. Experimental procedure

All corrosion experiments were conducted in an electric furnace attached to the glove box. BN crucible was selected as a corrosion cell due to its stability even with liquid Mg. By hanging the specimen, contact between the specimen and the bottom of the crucible was avoided to prevent any unpredictable reaction (Fig. 1). All corrosion experiments were conducted for 7 days at 700 °C.



Figure 1. Structure of the corrosion cell with transparent Quartz (left) and BN crucible (right)

### 2.2.1. Salt purification

The salt was purified chemically and electrochemically. To remove any gaseous impurities in the salt, Ar in the glovebox was purged by a bubbler. HCl gas (99.99%) diluted in Ar (99.996%) gas was used to reduce oxide ions and hydroxide ions into O<sub>2</sub> or H<sub>2</sub>O. Also, carbon tetrachloride (99.99%, Sigma Aldrich) was used for the same purpose. Metallic Mg (99.99%, Alfa Aesar) was used to residual H<sup>+</sup> ions chemically.

Three electrode cell was installed to analyze the salt condition. Tungsten wire (99.99%, Alfa Aesar) with 1 mm diameter was used as a working and counter electrode, and 1 wt% Ag/AgCl (99.999%, Alfa Aesar) reference electrode made by a thin quartz tube was installed. Versastat 3F and VersaStudio software (AMETEK SI) were used for the electrochemical analysis.

### 2.2.2. Reducing reagent addition

A cylindrical tube with a 4 mm inner diameter made by BN was used to confine liquid Mg. Eight holes were drilled at the bottom of the tube for the transfer of the electrolyte located inside and outside the tube.

### 2.2.3. Salt redox potential control

EuCl<sub>3</sub> (99.99%, Alfa Aesar) and EuCl<sub>2</sub> (99.99%, Sigma Aldrich) were used as a reagent. The electrochemical experiment was performed as described in Section 2.2.1.

## 3. Results and Discussion

A corrosion test for the 80Ni–20Cr specimen with NaCl–MgCl<sub>2</sub> without any additional purification process was conducted and the microstructure of the specimen is described in Fig. 2. Corrosion depth was about 30 μm.

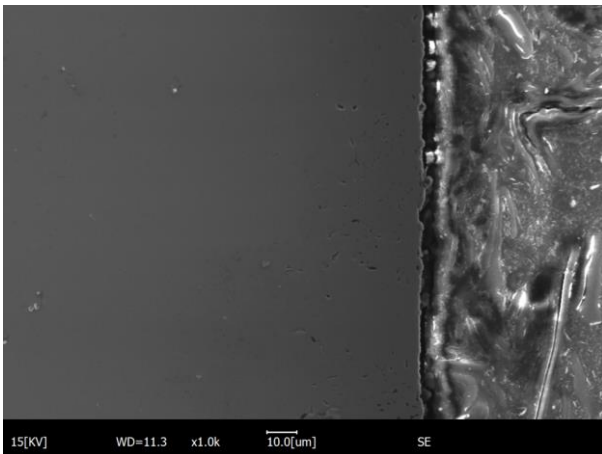
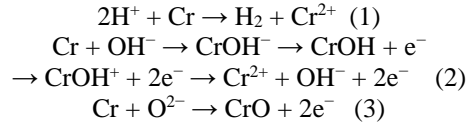


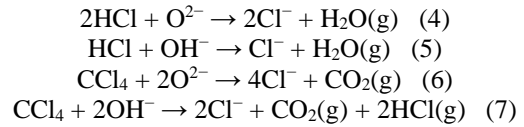
Figure 2. Microstructure of 80Ni–20Cr corroded in non-purified NaCl–MgCl<sub>2</sub> salt

### 3.1. salt purification

Residual moisture and oxygen in the molten salt may present as an ion state, but little amount of them can exist in a gaseous form such as H<sub>2</sub>O(g) and O<sub>2</sub>(g) and Ar gas was purged to remove these gaseous impurities. Ionic impurities induced these impurities may present in the form of H<sup>+</sup>, OH<sup>-</sup>, and O<sup>2-</sup> and these ions can accelerate corrosion by following reactions.



To remove these ions, HCl and CCl<sub>4</sub> were blown into the salt and the following are the expected reactions of them.



However, the H<sup>+</sup> ion cannot be reduced by purging the HCl or CCl<sub>4</sub> and two options can be applied to reduce the remaining H<sup>+</sup> into H<sub>2</sub>; the electrochemical method and the chemical method. As shown in Fig. 3, the cyclic voltammogram of the non-purified NaCl–MgCl<sub>2</sub> salt shows the cathodic peak for the H<sup>+</sup>/H<sub>2</sub> reaction at the 400 mV (vs. Ag/AgCl) region and anodic peak for the O<sup>2-</sup>/O<sub>2</sub> reaction at 1.1 V (vs. Ag/AgCl) region.

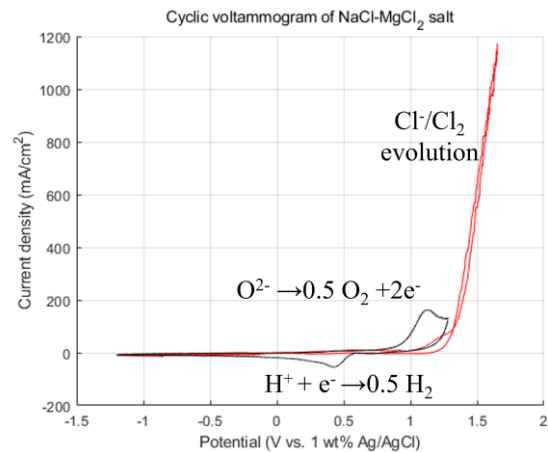


Figure 3. Cyclic voltammograms of NaCl–MgCl<sub>2</sub> salt before purification (black) and purified NaCl–MgCl<sub>2</sub> (red) (scan rate: 300 mV/s)

The remaining H<sup>+</sup> ion can be selectively reduced electrochemically by applying the potential for the H<sup>+</sup> reduction or chemically by introducing reducing metals such as Mg into the salt. After the purification process, the elimination of oxygen and hydrogen was confirmed

electrochemically. Within the purified salt whose residual moisture and oxygen were removed, the molten salt corrosion rate was effectively decreased.

### 3.2. Reducing reagent addition

One of the most promising techniques to mitigate molten salt corrosion is introducing the reducing reagent into the system. Magnesium which is the base element of the molten salt is much more reactive than alloying elements such as Ni, Fe, and Cr and oxidation of the sacrificial metal can suppress the electrochemical corrosion of the structural materials. 80Ni–20Cr alloy specimens were immersed into the pure NaCl–MgCl<sub>2</sub> salt with various metallic elements; Mg, Nb, Mo, and W.

The corrosion rate of the specimen was decreased by introducing the metallic Mg and Nb whose redox potential is more negative than alloying elements. Tungsten which is thought of as an inert element of molten salt corrosion did not show any different corrosion behaviors. The addition of molybdenum whose redox potential is more positive than Ni and Cr increased the corrosion rate of the specimen. Destructive corrosion of the specimen was observed when the liquid Mg escape the tube and attached to the specimen.

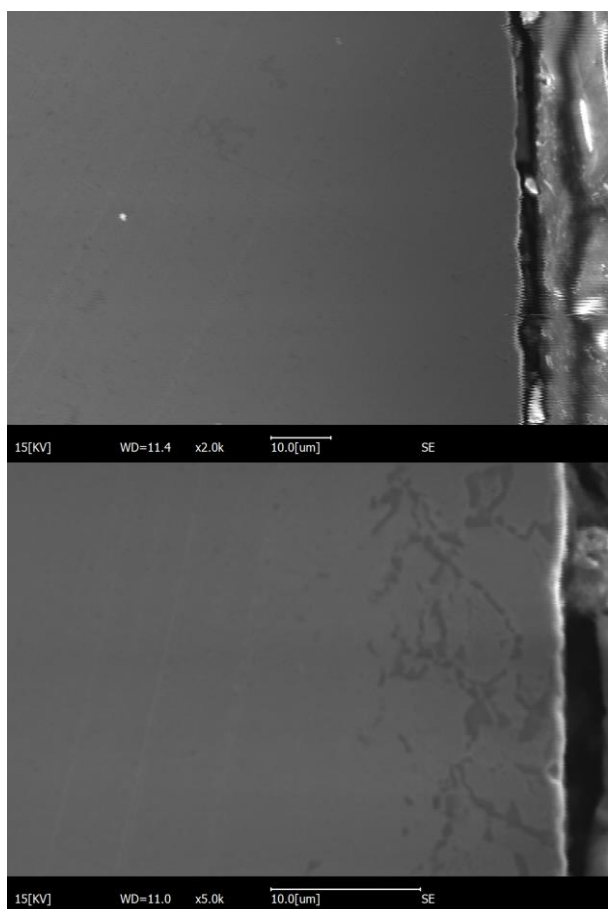
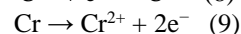
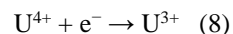


Figure 4. Microstructure of the corroded specimen with liquid Mg (top) and Mo (bottom)

### 3.3. Salt redox potential control

It is thought that various kinds of ions may exist in the MSR. Especially, uranium which the fissile element will exist in the form of U<sup>3+</sup> and U<sup>4+</sup> ion states in the salt system. In the fluoride system, it was confirmed that oxidizing the U<sup>4+</sup> ion accelerates the molten salt corrosion by the following reaction.



By controlling the salt potential, oxidizing ions can be reduced into less oxidizing ions. The salt potential control technique was examined in the fluoride system and showed that the corrosion rate could be reduced. However, this technique was not sufficiently examined in a molten chloride salt system. Europium trivalent ion and divalent ion are stable in molten NaCl–MgCl<sub>2</sub> salt and the redox potential of Eu<sup>3+</sup>/Eu<sup>2+</sup> is more positive than that of alloying elements and Eu<sup>2+</sup>/Eu<sup>0</sup> reaction cannot occur because the standard electrochemical potential of Mg is positive than that. Electrochemical behaviors of Eu<sup>3+</sup>/Eu<sup>2+</sup> in molten NaCl–MgCl<sub>2</sub> were analyzed (Fig. 5).

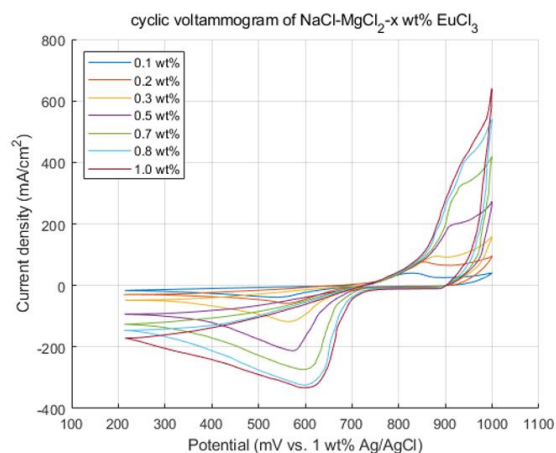


Figure 5. Cyclic voltammograms of molten NaCl–MgCl<sub>2</sub>–0.1–1.0 wt% EuCl<sub>3</sub> (scan rate: 500 mV/s)

The corrosion rate of the 80Ni–20Cr specimen was increased with EuCl<sub>3</sub> addition and was mitigated when the Eu<sup>3+</sup> ion was reduced into Eu<sup>2+</sup> ion. (Fig. 6)

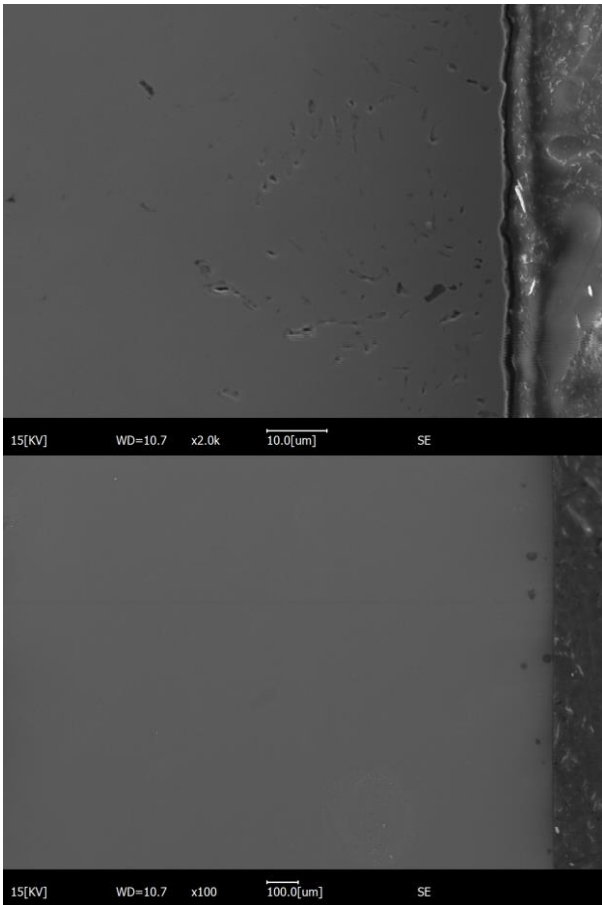


Figure 6. Microstructure of corroded specimen in molten NaCl–MgCl<sub>2</sub> salt with EuCl<sub>3</sub> (top) and EuCl<sub>2</sub> (bottom)

#### 4. Conclusion

In this study, various methods to mitigate molten salt-induced corrosion were investigated. Molten salt corrosion can be effectively mitigated just by removing residual moisture and oxygen from the salt. Reducing reagents such as liquid Mg can effectively mitigate the molten salt corrosion but should be adjusted carefully because contact between the structural material and liquid Mg can cause destructive corrosion. Also, the corrosion rate can be reduced by controlling the salt potential.

#### Acknowledgment

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