

Effect of metal-assisted chemical purification on corrosion in molten chloride salts of stainless steel

Hyeon-Geun Lee*, Jung-Min Kim, Taeho Kim, Daejong Kim

Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, Korea

*Corresponding author: hglee@kaeri.re.kr

1. Introduction

With the increasing focus on low-carbon energy, nuclear power plants have regained prominence. The next generation of nuclear reactors (Generation IV) has been designed to improve safety and sustainability compared to past reactors, and the Molten Salt Reactor (MSR) system is one of the most promising Gen IV reactors. Molten salt reactors have high safety features, such as passive cooling by molten salt and low-pressure operation, which can prevent severe accidents like fuel meltdown. Generally, fluoride and chloride molten salt are used as fuel and coolant systems in molten salt reactors. In the event of a severe accident, the safety of nuclear reactors can be guaranteed because the molten salts solidify. Nevertheless, the highly corrosive high-temperature molten salt during normal operation presents a significant challenge for MSR, and the corrosion issues of the reactor's structural materials must be solved.

Among the many research and development (R&D) programs for the development and deployment of MSR systems, the development and standardization of suitable structural materials is one of the most important limitations. The structural materials of MSR must exhibit corrosion resistance for molten salt, high-temperature strength, creep and fatigue resistance, and radiation resistance. The corrosion resistance of structural materials to molten salts is crucial to the development of the MSR system. Corrosion experiments in high-temperature molten salt environments have many difficulties due to the special properties of salts.

The presence of impurities such as oxygen, hydrogen, and carbon in chloride molten salt can greatly enhance the corrosion of structural materials. To enhance the corrosion resistance of the materials, the chloride molten salt must be purified prior to conducting corrosion experiments through thermal or chemical purification methods. In this study, the chloride salts were purified through heat treatment, followed by the addition of metal to the molten salt. The corrosion behavior of SS316L was evaluated for 100 hours at 650°C using chloride salts that were purified with different metals, and the effect of metal purification on corrosion was investigated

2. Methods and Results

The Molten Salt Reactor system under development by KAERI considers NaCl-MgCl₂ (57 mol. %:43 mol. %) salt as the molten salt. The eutectic temperature of mixed salts is 459 °C according to the phase diagram of NaCl and MgCl₂ [1]. To prepare the molten salt, NaCl (Sodium chloride, 99.5%, Junsei Chemical Co., Ltd.) and MgCl₂ (Magnesium chloride anhydrous, 99%, Alfa Aesar) powders are mixed and melted. However, due to the hygroscopic nature of chloride salts, the chloride powders adsorb H₂O on their surface, and the resulting molten chloride salt contains oxygen and hydroxide impurities. For the corrosion test of structural materials, pre-heat treatment at 300 °C was applied to remove absorbed hydroxide ion and oxygen.

In order to chemically purify the chloride salt, Mg, Zr, Al, and Zn metals were introduced into the salt and melted, and the mixture was maintained at 600°C for 48 hours. The metals chosen for chemical purification are those with a lower redox potential than Cr, which has the greatest impact on corrosion of structural metals. The metal added to the molten salt can remove oxygen in the form of metal oxide combined with oxygen in the molten salt. However, if these metals continuously react with chloride, it may lead to a change in the chemical composition of the molten salt, hence analysis of the salt is necessary.

The corrosion experiments with SS316L were conducted at 650 °C for 100 h using the molten chloride salts purified by the metals. Weight changes after exposure to each molten chloride salts for 100 h are shown in figure 1.

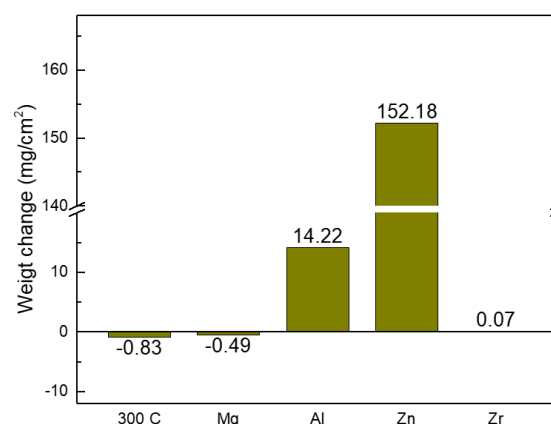


Figure 1. The weight loss of SS316L after the corrosion in molten chloride salts purified by metals.

Many studies have investigated the effectiveness of Mg for removing impurities from MgCl_2 -containing chloride salts and enhancing the corrosion resistance of metals via chemical purification[2-4]. In figure 1, it was seen that adding Mg for chemical purification improved the corrosion resistance of SS316 in the molten salt compared to thermal purification alone. Mg reacts with the hydroxide and O_2 present in chloride salt, resulting in the formation of MgO . This chemical reaction leads to purification of the molten salt, which in turn enhances the corrosion resistance of the system. SS316 specimens tested for corrosion in molten salt with Al, Zn, and Zr showed weight gain. The SS316 specimen in the molten salt with Zr exhibited a very low weight gain after corrosion, indicating limited progression of corrosion. However, in the molten salt containing Al and Zn, SS316 showed a very high weight gain after corrosion.



Figure 2. SS316 specimens after exposure to molten chloride salt purified by thermal, Mg, Al, Zn, and Zr, respectively.

The specimens after corrosion are shown in Figure 2. In the conditions of thermally purified molten salt and Mg-purified molten salt, the surface of the specimens showed little change after corrosion. Slight discoloration was observed on the surface of the specimens in the Zr purification molten salt condition. In the Al purification molten salt condition, it was observed that corrosion products were deposited on a part of the specimen, while slight discoloration was observed on the specimen surface in areas where corrosion products were not deposited. The weight increase after corrosion of SS316L under this condition is assumed to be mainly due to the corrosion products. In the condition of Zn purification molten salt, the surface of the SS316 specimen appeared very rough and there was a noticeable increase in the specimen's overall thickness. Based on the significant weight gain observed after corrosion, as well as the appearance of the specimen, it is hypothesized that a reaction occurred between the SS316 specimen and the Zn-containing molten salt, resulting in the formation of by-products on the specimen's surface.

To analyze the composition and impurities of the molten salt caused by the addition of metal, the chemically purified molten salt, which has been treated with metal, will be analyzed using TOF-SIMS.

The microstructure of the specimen surface was analyzed by SEM after the corrosion of the molten salt and shown in figure 3. In the thermal purification

molten salt specimens and Mg purification molten salt specimens, corrosion occurred at the grain boundary and pitting was observed, and some corrosion also occurred inside the grains. Grain and grain boundary corrosion were hardly observed in Al purification molten salt specimens and Zr purification molten salt specimens, and a layer with rounded particles was found on their surface. This indicates that the molten salt with added Al and Zr can create a passive layer with corrosion resistance on the surface of the SS316 specimen. The Zn purification molten salt specimen exhibited a porous and irregular surface, indicating that the molten salt reacted with the specimen, leading to the formation of a porous product on the surface, as seen by the photograph of the specimen surface.

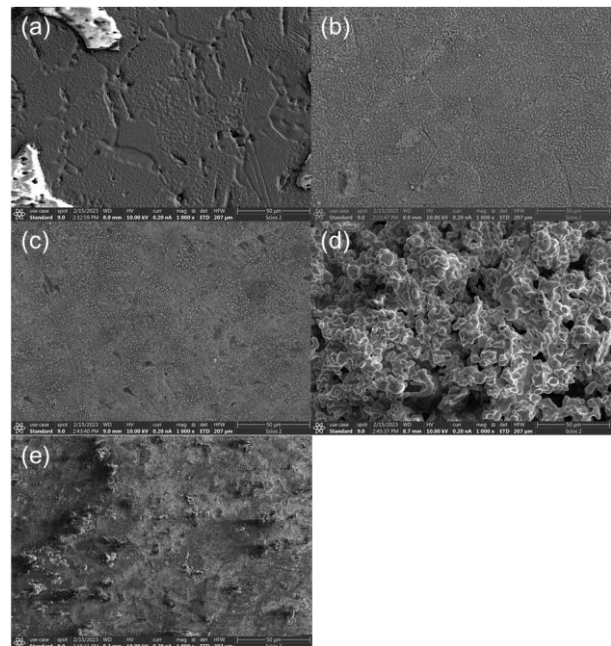


Figure 3. surface microstructure of corroded specimen in molten chloride salts purified by (a) thermal, (b) Mg, (c) Al, (d) Zn, (e) Zr.

To investigate the effect of each metal on the corrosion of SS316 in molten chloride salt, we will analyze the composition of the corroded surface using XRD and perform an elemental analysis of the cross-sectional surface after corrosion by SEM-EDS.

3. Conclusions

The present study aimed to investigate the corrosion behavior of SS316 in molten chloride salt that was chemically purified using Mg, Al, Zn, and Zr. To evaluate the effect of each metal on the corrosion behavior, we performed weight loss analysis and surface examination of the specimens. The results indicated that the corrosion resistance of SS316 was improved under the condition of purification by Mg, Al, and Zr. However, the chloride salts purified by Zr were found to

accelerate corrosion of SS316. After the corrosion in the chloride salt purified by Al and Zn, we observed a passive layer containing round particles on the surface of the specimens.

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