

Behavior of hydroxide impurity inside molten chloride salt solid after pre heat treatment

Hyeon-Geun Lee*, Daejong Kim

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

*Corresponding author: hglee@kaeri.re.kr

1. Introduction

Recently, with the emphasis on low carbon energy, nuclear power plants are in the spotlight again. The next generation (Generation IV) of nuclear reactor are designed to improve safety and sustainability compared to the past reactors, 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 so that prevent severe accidents such as fuel meltdown. Molten salt reactors use generally fluoride and chloride molten salt as fuel and coolant system. In the event of a severe accidents, the safety of nuclear reactors can be guaranteed because the molten salts are solidified, but the corrosion issues of the reactor structural materials must be solved due to the highly corrosive high temperature molten salt during normal operation.

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

Impurities such as oxygen, hydrogen, and carbon of chloride molten salt are very sensitive to corrosion of structural materials. Most of chloride salt have high hygroscopic properties. The corrosion properties may be changed by oxygen from the hydroxide adsorbed on the salt in the corrosion test of structural materials. In this study, oxygen and hydroxide impurity change inside the chloride salt solid due to the pre-heat treatment before melting of salt are investigated.

2. Methods and Results

Molten Salter Reactor system being developed by KAERI considers NaCl-MgCl₂ (57 mol.% : 43 mol.%) salt as molten salt. The eutectic temperature of mixed salts is 459 °C according to the phase diagram of NaCl and MgCl₂[1]. NaCl (Sodium chloride, 99.5%, Junsei Chemical Co., Ltd.) and MgCl₂ (Magnesium chloride anhydrous, 99%, Alfa Aesar) powder are mixed and melted to prepare molten salt. Due to the hygroscopic properties of chloride salt, the chloride powders have

the adsorbed H₂O on their surface, the molten chloride salt have oxygen and hydroxide impurities inside. For corrosion test of structural materials on molten salt, pre-heat treatment of chloride powders was required to remove adsorbed hydroxide ion.

In order to confirm the appropriate pre-heat treatment condition, DSC and TGA of mixed salts and each salt were carried out. The heating rate was set as 3 °C/min. Through the analysis of DSC and TGA, a large weight loss and endothermic reaction were observed around 250 °C. A slight decrease in mass occurred as the temperature increased in NaCl and MgCl₂ mixed powder up to 400 °C. The H₂O adsorbed on the power surface was thought to be hydrolyzed as the temperature increased.

Pre-heat treatment is required to purify the molten chloride salts. According to the hydrolysis of MgCl₂·6H₂O, the following reaction occurs depending on the temperature:

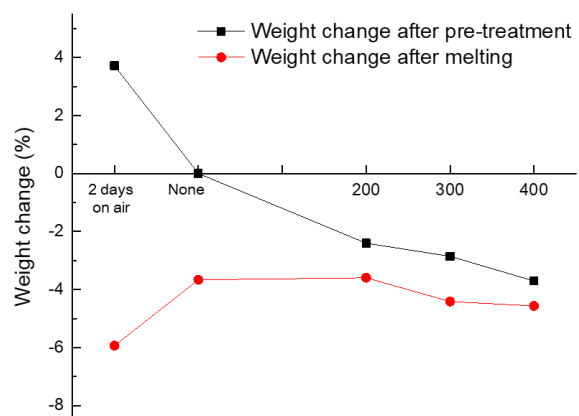
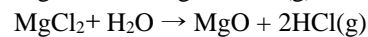
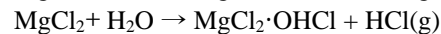
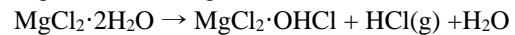
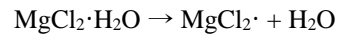
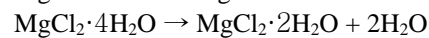


Fig. 1. Weight change after pre-treatment and melting of mixed salts.

After 200, 300, 400 °C pre-heat treatment and 2 days on air, the weight change of mixed salts was measured and the hydroxide or oxygen impurities in the solidified mixed molten salts were evaluated. In fig. 1 the weight

change of mixed salts were shown after pre-treatment. Weight loss of mixed salts slightly increased as increase pre-heat treatment temperature from 200 °C to 400 °C. It was confirmed that H₂O adsorbed to mixed chloride powder was being removed through pre-heat treatment. The mixed powder pre-treated for 2 days at room temperature showed an increase in weight of about 4%, which is because moisture in the air was adsorbed to the powder surface.

As a result of measuring the change in weight after melting each sample, all samples showed weight loss. The specimens pre-heated at 200 °C had almost the same weight loss after melting as the untreated specimen. Specimens pre-heated at above 300 °C showed an increase in weight loss after melting compared to the untreated specimen. As confirmed from the TG-DSC results, pretreatment requires a temperature of 250 °C or higher in order to sufficiently remove the adsorbed H₂O.

The weight loss was the highest in the specimen that had already adsorbed a lot of H₂O at room temperature. When the adsorbed H₂O is not sufficiently removed and heated to the melting temperature in the mixed chloride powder, additional reactions between the powder and adsorbed H₂O may occur near the melting temperature. The impurities and by-products in the molten chloride salt were analyzed through ToF-SIMS analysis.

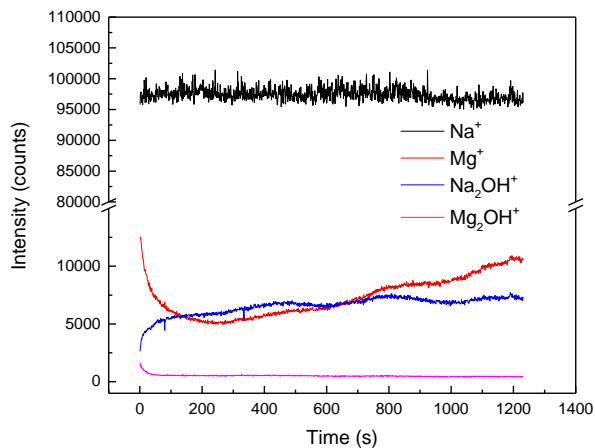


Fig. 2. ToF-SIMS depth profile of the NaCl-MgCl₂ mixed salts pre-heated at 400 °C.

ToF-SIMS depth profile of the solidified salts pre-heated at 400 °C after melting was shown in fig. 2. Sodium hydroxide ion increased as sputtering time increased. Magnesium hydroxide ions were slightly detected at the surface and decreased as they progressed in depth direction, maintaining small amounts. Sodium hydroxide and magnesium hydroxide impurities are observed to remain in molten salts despite the pre-heat treatment at 400 °C.

ToF-SIMS results of 200, 300 °C pre-heat treatment specimen and 2 days pre-treat specimen at room

temperature will be analyzed in terms of the hydroxide impurities.

3. Conclusions

The impurities of molten chloride salts used in MSR system were studied. NaCl-MgCl₂ mixed chloride salts melt in the eutectic temperature and they may have hydroxide or oxygen impurities due to the hygroscopic properties of chloride powders. Based on the DSC-TG experimental results, mixed chloride powders were pre-treated at 200, 300, 400 °C. Weight loss of molten chloride salts increased as pre-heat treatment temperature increased from 200 to 400 °C by removing the adsorbed H₂O. Sodium hydroxide and magnesium hydroxide impurities were observed in solidified chloride salts by ToF-SIMS.

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