Corrosion behaviors of Ni-based alloy in molten NaCl–MgCl₂ salt with a cyclic temperature system

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1. Introduction

A molten salt reactor (MSR) is one of the promising GEN-IV reactors which uses molten salt as its fuel and coolant. The most challenging aspect of the MSR development is molten salt corrosion. Molten salt is very corrosive to the structural material and various experiments to analyze molten salt corrosion were conducted. Most of the corrosion experiments were conducted at static temperature systems because of their aims. [1, 2]

The temperature range of the primary coolant of the chloride-based molten salt reactor is expected to be about 550–750 °C. In general, it is known that the molten salt corrosion is accelerated as the temperature increases and vice versa. Also, an increment of structural material ions in the molten salt decelerates the molten salt corrosion. Therefore, it is unreasonable to apply the results of the corrosion experiment performed at a constant temperature to the MSR environment. In order to understand the corrosion effect by temperature, many researchers conducted experiments using passive or active circulation loops. [3, 4]

The loop system is thought as the best option to analyze the corrosion behaviors with the temperature changes, but there are several problems. Usually, the scale of the loop system is very large, and it is difficult to control the environment. Also, various sensors to monitor the temperature or oxygen content of the salt and purification devices need to be installed in the loop and these components can introduce additional corrosion between dissimilar alloys. Additionally, it is hard to obtain high-purity salt without moisture and oxygen contamination during and after the experiment if the loop is not installed in an inert atmosphere environment.

Therefore, in order to understand the corrosion behavior of the structural material according to the temperature, an experiment was performed in which the temperature of pure NaCl–MgCl₂ molten salt was changed to 700 °C and 550 °C at regular intervals and the specimen was replaced at the same time. Microstructural changes and the weight difference were analyzed by SEM–EDS and a high-accuracy electronic scale.

2. Experimental Setup

2.1. Experimental equipment

All corrosion experiments and reagent preparation processes were carried out within a glovebox filled with Ar (99.996%). Moisture and oxygen of the Ar gas were captured by a purification system installed in the glovebox and their contents were not exceeded 0.1 ppm during the experiments.

Eutectic NaCl–MgCl₂ salt was prepared by mixing NaCl (Alfa Aesar, 99.99%) and MgCl₂ (Alfa Aesar, 99.99%). Both NaCl and MgCl₂ were preheated at 200 °C, 400 °C, and 600 °C sequentially for 24 hours each to remove residual moisture and oxygen. Also during the preparation process, oxidative compounds such as magnesium hydroxychloride (MgClOH) decomposed into non-reactive magnesium oxide (MgO) by the following reaction.

$MgOHCl \rightarrow MgO + HCl (550 \ ^{\circ}C) (1)$

The 80Ni–20Cr alloy was selected as the specimen material for the corrosion experiment. The specimen was cut by waterjet (T500 3015 hybrid, TOPS) to minimize mechanical shock to the specimen. Specimen was polished with 400-girt sandpaper and finalized with 1-micrometer Al₂O₃ paste. Before and after the experiment, the specimen was placed in a 50 ml vial containing distilled water and rinsed using an ultrasonic cleaner, dried in a vacuum chamber to prevent oxidation, and weighed with a high-accuracy electronic scale. The temperature was controlled by an electrical furnace with a PID controller and was confirmed that less than 20 minutes was taken to change the salt temperature from 550 °C to 700° C, or from 700 °C to 550 °C.

2.2. Experimental procedure

15.000 g of pure eutectic NaCl–MgCl₂ salt was used as the corrosive salt for each experiment. Experiments were conducted with 3 conditions; the temperature was constant at 550 °C and 700 °C and temperature changes between 550 °C and 700 °C with regular intervals.

Schematics of the corrosion experiment for the cyclic temperature condition is described in Fig. 1 and the specimen and temperature condition are described in Fig. 2. Two specimens were placed above the molten salt and the H-cycle specimen was introduced to the molten salt at 700 °C for 7 hours and ejected from the salt. After the salt temperature decreased to 550 °C, the

C-cycle specimen was injected into the molten salt for 3 hours and ejected. After 10 cycles, the corrosion experiment with cyclic temperature condition was finished.



Figure 1. Schematics of corrosion experiment with temperature change



Figure 2. Specimen loading condition regards the salt temperature during the corrosion experiment with temperature change

Corrosion experiments with constant temperature conditions were conducted to compare that with cyclic temperature condition, and thus, loading and unloading of the specimens were performed repeatedly. For the 700 °C condition, 10 times of 7-hours-loading–1-hour-unloading were carried out and 10 times of 3 hours loading-1 hour unloading were carried out for the 550 °C condition.

3. Results and Discussion

Weight changes after the corrosion experiments are reported in Table 1. Weight loss occurred during the corrosion experiments with constant temperature (Hrepeat, C-repeat). After the corrosion experiment with cyclic temperature condition, only the weight of the specimen that was exposed to higher temperature decreased and the specimen exposed to lower temperature gained some weight.

Table 1. Weight change of specimen after corrosion experiment

Test ID	Weight change	Note
	$(\mu g/cm^2)$	
H-repeat	-5520.3	Constant temperature
I		(700 °C)
C-repeat	+371.6	Constant temperature
-		(550 °C)
H-cycle	-2121.6	Cyclic temperature
•		(700 °C)
C-cycle	-162.2	Cyclic temperature
-		(550 °C)

Figure. 3 and 4 show the SEM images of the H-repeat and C-repeat specimens. Corrosion depth was analyzed as 20 μ m for the H-repeat specimen and 2–3 μ m for the C-repeat specimen. The H-repeat specimen shows about 10 times deeper corrosion depth than the C-repeat specimen and this result is also well-matched with the weight loss data (Table. 1).



Figure 3. SEM images of the H-repeat specimen



Figure 4. SEM images of the C-repeat specimen

The corrosion depth of the H-cycle specimen which was immersed in 700 °C molten salt with cyclic temperature condition was analyzed as 50 μ m (Fig. 5). However, the C-cycle specimen did not show any corrosion and even reduced-Cr was identified.



Figure 5. SEM images of the H-cycle specimen



Figure 6. SEM images of the C-repeat specimen (left: SE image, right: BSE image)

Chromium is the oxidizing element of the 80Ni-20Cr specimen and continuous Cr dissolution was reported. During the high-temperature molten salt environment, corrosion occurred in which Cr in the H-cycle specimen is eluted into the molten salt phase, increasing the Cr^{2+} ion concentration in the salt. Even if the temperature of the molten salt is lowered while the specimen was withdrawn, the eluted Cr²⁺ ions are expected remaining its state in the salt since the solubility of CrCl₂ in the NaCl-MgCl₂ salt is very high. When the C-cycle specimen was loaded into the molten salt, the Cr²⁺ ion in the salt was reduced in the process of achieving an electrochemical equilibrium between the Cr^{2+} ion in the molten salt and Cr in the specimen. Some of the reduced Cr was observed on the surface of the specimen and some of it was located at the bottom of the container.

As can be seen in Table 1, the weight change of the H-repeat specimen and the C-repeat specimen differs by about 13 times. From this result, the electrochemical equilibrium with the specimen may occur in a relatively

low Cr^{2+} concentration when the temperature of the salt is low. Therefore, when the corrosion experiment is performed with the temperature change, it can be inferred that oxidation of the specimen occurs during the salt temperature is high and oxidized ion in the salt is re-reduced when the temperature is low. Since these processes were repeated, the weight loss of the H-cycle specimen is 2.6 times larger than that of the H-repeat specimen.

4. Conclusion

In this study, corrosion behaviors of 80Ni–20Cr alloy in molten NaCl–MgCl₂ salt with temperature change were investigated. It is obvious that temperature change can accelerate molten salt corrosion. Therefore, in addition to analyzing the corrosion phenomenon at a constant temperature condition, it is judged that additional research on corrosion under various temperature change conditions is absolutely necessary.

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