Corrosion mechanism analysis of Ni and Ni model alloy on molten chloride salt

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1. Introduction

The next generation of nuclear reactors is being designed with a focus on enhancing both safety and sustainability, surpassing the capabilities of their predecessors. Among the most promising of these advanced designs is the Molten Salt Reactor (MSR) system. MSRs offer substantial safety advantages, including passive cooling through molten salt and low-pressure operation, which together significantly reduce the risk of severe incidents, such as fuel meltdown. Typically, fluoride and chloride-based molten salts are utilized as both fuel and coolant in these reactors. In the unlikely event of a severe accident, the inherent safety of the reactor is further bolstered by the ability of molten salts to solidify upon cooling.

However, a key challenge for MSRs lies in the highly corrosive nature of molten salts at elevated temperatures during normal operation. Addressing the corrosion of reactor structural materials is essential for the successful deployment of MSR technology. The development and standardization of appropriate structural materials represent a critical hurdle. These materials must demonstrate exceptional corrosion resistance to molten salts, along with high-temperature strength, resistance to creep and fatigue, and radiation tolerance. Among these, corrosion resistance to molten salts is particularly crucial for advancing the MSR system.

This study aims to develop a Ni-based alloy with enhanced resistance to molten salt corrosion. To achieve this, we explored the impact of various metal elements—commonly used in the chemical purification of molten salts—on the manufacturability and performance of Ni alloys. The corrosion behavior of the prepared Ni alloy was evaluated in molten salt environments, and the results were analyzed to assess the influence of alloying elements on the alloy's corrosion resistance in such conditions.

2. Methods and Results

Molten chloride salt of $NaCl\text{-}MgCl_2$ is selected for the corrosion mechanism analysis in Ni and Ni alloy. $NaCl\text{-}MgCl_2$ (57 mol.%:43 mol.%) mixed salt's eutectic temperature is 459 ºC, as indicated by the NaCl and MgCl2 phase diagram.[1] . For the molten salt corrosion experiments, NaCl (Sodium chloride, 99.5%, Junsei Chemical Co., Ltd.) and $MgCl_2$ (Magnesium chloride anhydrous, 99%, Alfa Aesar) powders are mixed and melted after heat treatment at 300 ºC for thermally purifying. Thermal purification step was applied to remove absorbed hydroxide ion and oxygen in as-received salt powder. Following the melting of the mixed salt, a chemical purification phase was introduced, involving the use of Mg pieces[2-4]. This purification step was conducted at 550°C for a duration of 48 hours

To investigate the corrosion mechanism Ni and Ni alloy, Ni and Ni alloys which have Cr, Mo, W as allying element were prepared by a vacuum arc melting (VAR) and cold rolling. 200g master ingot was melted heat treated at 1200 ºC for 2 hr. The sheets of Ni and Ni alloys with a thickness of about 1.5 mm were produced by cold rolling. The molten salt corrosion specimens were cut from the alloy sheets with the dimensions 15 x 10 x 1 mm^3, grinded down by grit #1000 silicon carbide papers.

Table 1. The composition of Ni and Ni model alloy

Number	Ni	Cr	Mo	W	비고
1	100				
2	90	10			
3	80	10	10		
4	80	10		10	
5	90		10		
6	90			10	
7	90	10			C<0.05
8	80	10	10		C<0.05
9	80	10		10	C<0.05

To investigate the effect of Cr, Mo and W used as solid solution strengthening elements, samples were prepared by adding 10 wt.% of each solid solution strengthening element to Ni, and the detailed alloy compositions are shown in Table 1[5-6]. XRD analysis of each specimen showed that they were all analyzed as Ni single phase, confirming that all alloying elements were well employed in Ni, and the Ni peak was shifted to the left depending on the employed element. Microstructural analysis of each specimen showed that the Ni alloys with alloying elements exhibited smaller grains than pure Ni, with the Mo-added specimen exhibiting the smallest grain size. Carbide precipitation were observed in Ni alloys with carbon, more carbide appeared inside the specimen than on the surface.

Molten salt corrosion tests were conducted for 200 hours at 700°C using Ni and Ni-based model alloys within a glove box system under an Ar atmosphere. Oxygen levels were maintained below 50 ppm, and moisture levels were kept below 5 ppm throughout the experiment. Weight loss was observed in all specimens after corrosion testing. Table 2 presents the weight loss values for each specimen. Pure Ni specimens exhibited a significant value of weight loss, indicating that Ni is susceptible to corrosion, likely due to the presence of oxygen or impurities in the molten salt. The corrosion results for specimens containing Cr, Mo, and W in the Ni matrix respectively showed that the Ni-Cr alloy had a higher weight loss than pure Ni, while the addition of Mo and W enhanced corrosion resistance when incorporated into Ni. In the Ni-Cr alloy system, specimens with Mo and W additions demonstrated a significant improvement in corrosion resistance compared to the Ni-Cr alloy alone. This confirms that Mo and W, when alloyed with Ni, contribute to improved resistance against molten salt corrosion in Ni or Ni-Cr alloys.

Table 2. Molten chloride salt corrosion results at 700 ^{o}C for 200h of Ni and Ni model alloy specimen.

Specimen	Weigh loss	Stdev
1	-2.718	0.174
2	-3.393	0.289
3	-2.024	0.261
4	-1.992	0.152
5	-1.770	0.329
6	-1.583	0.716
7	-1.450	0.231
8	-1.504	0.182
9	-1.739	0.003

In the specimens where carbon was added to the Ni alloy to form precipitates, the addition of Mo and W did not significantly improve corrosion resistance. The cross-section microstructure of each specimen after molten salt corrosion was analyzed to further investigate the effects of Cr, Mo, and W element on the corrosion mechanisms of the Ni alloy.

3. Conclusions

The molten salt corrosion mechanism of pure Ni metal and Ni alloys employing Cr, Mo, and W on Ni metal was analyzed. In a 700 degree NaCl-MgCl2 molten salt corrosion atmosphere, all specimens exhibited weight loss. It was found that the weight loss increased when Cr was incorporated into Ni, and Mo and W improved the corrosion resistance when incorporated into Ni. Cross-sectional microstructure analysis after molten salt corrosion confirmed the effect of Cr, Mo, and W on molten salt corrosion.

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