Effect of alloying element in nickel alloy on molten chloride salt corrosion

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1. Introduction

The next generation of nuclear reactors has been designed to improve safety and sustainability compared to past reactors. Molten Salt Reactor(MSR) system is one of the most promising next generation 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. 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.

In this study, the goal is to produce a Ni alloy that exhibited high molten salt corrosion resistance. In order to improve the molten salt corrosion resistance, we investigated the metal elements used in the chemical purification of molten salt and determined the influence of each element on the manufacturability of Ni alloys. Molten salt corrosion of the prepared Ni alloy was performed and the results were analyzed to investigate the effect of alloying elements on molten salt corrosion resistance.

2. Methods and Results

NaCl-$MgCl_2$ (57 mol.%:43 mol.%) mixed salt which is considered for base salt of the molten salt reactor system developed by KAERI was used for molten salt corrosion evaluation. This mixed salt's eutectic temperature is 459°C, as indicated by the NaCl and $MgCl_2$ phase diagram.[1] To assess molten salt corrosion, a series of experiments were conducted. 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 metallic pieces. This purification step was conducted at 600°C for a duration of 48 hours. Specifically, metals such as Mg, Zr, and Al were chosen [2-5]. These metals were selected due to their lower redox potentials compared to Cr, which is known to have a significant impact on the molten salt corrosion of structural materials. The inclusion of these metals in the molten salt facilitated the removal of oxygen through the formation of metal oxide compounds with the oxygen present in the molten salt.

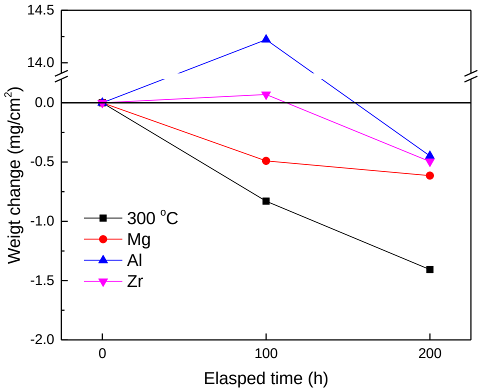


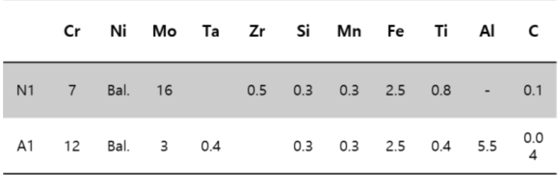
Fig. 1. Weight changes of SS316H specimen after exposure to molten chloride salts purified by Mg, Al, and Zr

The chemical purification using Mg is mainly used during the pretreatment process of molten salt, however the specific influence of the metal-involved chemical purification step on the corrosion behavior of metals in molten salt remains unclear. In this study, the corrosion experiments with SS316H were conducted at 650 ºC for 100, 200 h using the molten chloride salts purified by Mg, Zr, and Al. Weight changes and Cr depletion depth after exposure to each molten chloride salts are investigated. Fig. 1 shows the weight changes of the SS316 specimen versus elapsed time in molten chloride salt. it was seen that adding Mg, Al, Zn for chemical purification improved the corrosion resistance of SS316 in the molten salt compared to thermal purification alone. Metal pieces can react with the hydroxide and O_2 present in chloride salt, resulting in the formation of oxide. This chemical reaction leads to purification of the molten salt, which in turn enhances the corrosion resistance of the system.

It was observed that corrosion products were deposited on some of the specimens under Al and Zr purified molten salt conditions for 100 h, which seems to have caused slight weight gain. As a result, in addition to Mg, which is a component such as salt, the effect of chemical purification of Al and Zr was confirmed. Based on this, we tried to analyze the effect of minute elements such as Al and Zr on molten salt corrosion resistance when manufacturing a Ni-based new alloy. It has been reported that in alloys containing Al, corrosion resistance can be improved by forming an Al_2O_3 protective film in molten chloride salt corrosion environments.[6] However, large additions of Al in Ni alloys can lead to poor mechanical properties and manufacturability due to the formation of NiAl intermetallic phases, so the preparation of Al-added Ni alloys should be done with caution. Zr is a commonly used element in Ni alloys to improve mechanical properties, and there are reports of very small amounts being added to improve tensile strength by changing the geometry of the grain boundaries or precipitates within the grain.[7-8]

In this study, To analyze the effect of trace element addition of Al and Zr on molten salt corrosion in Ni alloys, Ni alloys with the composition shown in Table 1 were prepared by melting. A 50 kg master ingot was prepared in a vacuum induction melting (VIM) furnace. The master ingot was cut into some pieces after homogenization heat treatment at 1177 ^{o}C. The sheets of Ni alloys with a thickness of 1.5 mm were produced at 1100 ^{o}C by hot rolling. A1 specimen is difficult to be rolled due to their high hot cracking susceptibility. The manufacturability of Al specimens was investigated through various hot rolling conditions. Finally, all the alloys were solution heat treated at appropriate temperature at 30 min, followed by quenching in water. 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 #1200 silicon carbide papers.

Table 1. Molten salt corrosion resistivity Ni alloy composition (wt.%)



	Cr	Ni	Mo	Ta	Zr	Si	Mn	Fe	Ti	Al	C
N1	7	Bal.	16		0.5	0.3	0.3	2.5	0.8	-	0.1
A1	12	Bal.	3	0.4		0.3	0.3	2.5	0.4	5.5	0.04

The microstructure of Ni alloys with Al and Zr additions was analyzed as a function of rolling and heat treatment conditions. The microstructure of each specimen and the molten salt corrosion resistance due to the addition of alloying elements were studied. The weight change and Cr depletion layer after 200 to 500 h immersion corrosion at 650 ^{o}C were evaluated, especially the protective film due to Al.

3. Conclusions

The present study analyzed the effect of metal elements on chemical purification in molten salt corrosion, and the effect of adding Al and Zr, which have shown high effectiveness in chemical purification, to Ni alloys was investigated. The hot rolling process and heat treatment process were optimized to produce Ni alloys with Al and Zr additions, respectively. The as-prepared Ni alloys were subjected to molten salt corrosion at 650 oC to determine the effect of Al and Zr on molten salt corrosion in Ni alloys.

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