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Development strategy of molten chloride salt corrosion resistive Ni superalloy

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1. Introduction

The next generation of nuclear reactors aims to enhance safety and sustainability compared to predecessors, with the Molten Salt Reactor (MSR) system standing out as one of the most promising options. These reactors boast high safety features, such as passive cooling by molten salt and low-pressure operation, which can prevent severe accidents like fuel meltdown. Typically, fluoride and chloride molten salts are utilized as fuel and coolant systems in MSR. In case of a severe accident, the solidification of molten salts ensures the reactor's safety. However, the highly corrosive nature of high-temperature molten salt during regular operation poses a significant challenge for MSR, necessitating the resolution of corrosion issues in the reactor's structural materials. Developing and standardizing suitable structural materials is a crucial limitation. These materials must exhibit corrosion resistance to molten salts, as well as high-temperature strength, creep and fatigue resistance, and radiation resistance. The corrosion resistance of structural materials to molten salts is vital for the advancement of the MSR system. Therefore, the development of materials for use in MSR structures is being researched in many countries.

In this study, material development strategy for MSR structural materials in KAERI was introduced. Ni-Cr-Mo superalloy is generally known as high corrosion resistive material at high temperature air environments and high temperature molten salts environments. Based on the Ni-Cr-Mo alloy, we designed the alloy using two main concepts. The first is to adjust the corrosion-resistant elements to improve the corrosion resistance of the Ni alloy itself, and the second is to form an Al_2O_3 layer on the surface with excellent corrosion resistance. We have studied the improvement of high-temperature mechanical properties and creep properties by microstructure modification in Ni alloys with excellent corrosion resistance.

2. Methods and Results

High-temperature corrosion-resistant Ni alloys were prepared by two design strategies: improving the corrosion resistance of the Ni alloy itself and forming a corrosion-resistant film. 1 - 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 1000~1200 ºC. The sheets of Ni alloys with a thickness of about 1.5 mm were produced at 1000~1200 ºC by hot rolling. All the alloys were solution heat treated at appropriate temperature at 1 hr, followed by cooling method(water quenching, air cooling, furnace cooling, etc). 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.

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 Mg pieces[2-4]. This purification step was conducted at 550°C for a duration of 48 hours

M1 alloy, which has an increased proportion of Mo to resist molten salt corrosion in Ni alloy, and A1 alloy, which has a certain amount of Al added, were prepared in 70 kg batches[5-6]. The M1 alloy was subjected to solid solution heat treatment at each temperature and then cooled, and the tensile properties at room temperature and high temperature as a function of cooling method and temperature are shown in Figure 1. M1 alloy is an alloy with increased Mo as a solid solution strengthening element, which shows high yield strength at high temperature and room temperature. The Mo element is known to cause the formation of the Sigma phase in Ni alloys, which reduces high temperature strength and ductility. In Figure 1, the strength and ductility at room temperature are shown to be proportional to the heat treatment conditions in M1 alloy with high Mo content. At 700 ºC, the strength and ductility of M1 alloy increased simultaneously according to the heat treatment condition. The microstructure of M1 alloy was analyzed to understand the reason for the increase in ductility.

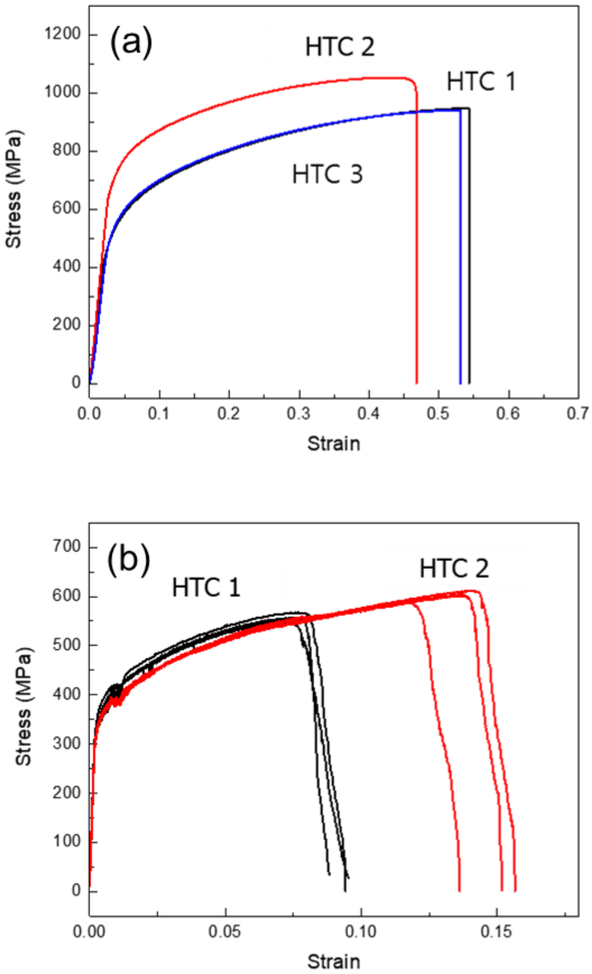

Fig. 1. Strain-Stress curves of M1 alloy at (a) room temperature, (b) 700 °C

A1 alloys have a very high strength due to gamma' because of the high aluminum content added. Tensile evaluation at room temperature showed an inverse relationship between strength and elongation with heat treatment. The tensile test evaluation of A1 alloy at 700 °C showed that the elongation varied significantly depending on the heat treatment condition of the specimen, and the microstructure of each specimens was analyzed.

Table 1. Molten chloride salt corrosion results at 700 °C for 200 h of M1 and Hastelloy N specimens

	Hastelloy N	M1 - HTC 1	M1 – HTC 2
Weigh loss after molten salt corrosion	1.52 mg/cm^2	1.07 mg/cm^2	1.27 mg/cm^2

The 200 h molten salt corrosion results at 700 °C of M1 specimen with different heat treatment condition and Hastelloy N specimens are shown in Table 1. All specimens showed weight loss after molten salt corrosion. The M1 specimens with more Mo showed slightly less weight loss than the Hastelloy N specimens. The microstructure evaluation after molten salt corrosion of M1 specimens with different heat treatment conditions was performed to analyze the molten salt corrosion mechanism in Ni alloys with high Mo addition. The molten salt corrosion evaluation of the A1 specimen is ongoing and will be analyzed.

Ni model alloys were prepared to optimize the composition of Mo and W in order to develop Ni alloys with excellent corrosion resistance in chloride molten salt environments[7-8]. The total addition of Mo and W in the Ni alloy was set to 18 wt.% or less. Through thermodynamic calculations, the model alloy was designed by selecting the composition conditions to minimize precipitates that can adversely affect the high-temperature mechanical properties at the target temperature of 700 °C. Each model alloy was evaluated for molten chloride salt corrosion at 700 °C, and the Ni alloy with the optimized Mo/W ratio with the best corrosion resistance was selected. Each specimen will be evaluated for high temperature mechanical properties according to the heat treatment conditions.

3. Conclusions

To develop Ni alloys as high-temperature structural materials with excellent molten salt corrosion resistance, model alloys were prepared and evaluated by adding corrosion-resistant elements to a basic Ni-Cr-Mo alloy. Room and elevated temperature tensile evaluations were performed on specimens with significantly increased amounts of Mo to improve corrosion resistance. Ni alloys with an increased amount of Mo showed improved corrosion resistance in the molten salt corrosion at 700 °C Ni model alloys with Al added to form a corrosion-resistant protective film and Ni model alloys with an optimized ratio of Mo to W were prepared and tested for tensile properties and molten salt corrosion.

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