A Study on Thermodynamic Corrosion Behavior of Structural Material in Chlorine-Based Molten Salt Reactor

Jisu Na [a], Unho Lee [a], and Young Soo Yoon [a]*
[a]Department of Materials Science and Engineering, Gachon University, Gyeonggi-do,13120
[*]Corresponding author: benedicto@gachon.ac.kr

1. Introduction

IPCC (Intergovernmental Panel on Climate Change)'s Net-zero and RE100 policies strongly regulate CO_2. Nuclear power, which does not generate CO_2, is a renewable energy source that complies with the policy. Among them, the 4th-generation nuclear power plant MSR is attracting a lot of attention around the world because of its advantages of stability and high thermal efficiency due to the low vapor pressure [2]. Fluorine-based salts are mainly used as molten salts, while chlorine-based salts with operating temperatures of 500~600°C, which are about 100°C higher than fluorine-based salts, are also emerging as promising molten salt candidates. In order to apply chlorine-based MSR, several conditions are required. First, mechanical strength for application as a structural material, Second, securing thermal shock resistance at high operating temperature, and finally, corrosion resistance by chlorine ions is required. However, it is difficult to predict the operating environment because there have been no actual commercialization cases of chlorine-based MSR [3-4]. Other studies have demonstrated the necessary ranges for melting point, yield strength, tensile strength, etc. in operating environment simulations and provided several candidate materials.

Table.1. Mechanical properties as MSR structural materials

	Stainless Steel 316L	Hastelloy C-276	Hastelloy N10003
Melting Range	1400℃	1370℃	1400℃
Tensile Strength	550 MPa	727 MPa	800 MPa
Elongation	40%	70%	51%
Thermal conductivity	15.0 W/m℃	21.9 W/m℃	23.6 W/m℃
Thermal expansion	16.5 um/m℃	14.1 um/m℃	14.9 um/m℃
Yield Strength	205 MPa	313 MPa	316 MPa
Hardness	95 HRB	87 HRB	96 HRB

Based on the simulation results, we aimed to commercialize next-generation nuclear reactor by providing an environment similar to chlorine-based MSR to the candidate structural materials and finding an appropriate alloy. For application in chlorine-based MSR, an alloy with a minimum Fe content is a necessary condition. Iron-based alloy is not suitable because $FeCl_3$ is easily formed through chlorine-based oxidation. If Fe is not contained, the hardness of mechanical strength is weakened. Especially, nickel-based alloys lacking in hardness require a minimum amount of Fe. It is necessary to confirm the structural stability and interaction effect of the addition of trace elements to structural materials. In this study, structural alloy materials with excellent oxidation resistance in chlorine-based salts containing elements such as Mo, Cr, Ni, and Fe was selected as a candidate group [5]. The selected candidates include Iron-based Stainless Steel with high mechanical strength and Hastelloy®, nickel-based metal with a representative chlorine corrosion resistance. After that, the structural material showing high stability among them will be applied to the long-term operation of the MSR.

2. Methods and Results

2.1 Materials and corrosion immersion test

Stainless Steel 316L, Hastelloy® C-276, and Hastelloy® N10003 metal alloy plates were cut and standardized to 1 cm^2 for chlorine-based mixed salt immersion testing. After the rinsing process, three candidate structural materials in an alumina crucible were reacted with 0.506M NaCl – 0.494M KCl mixed chlorine salt [1], which has a melting point of 657℃.

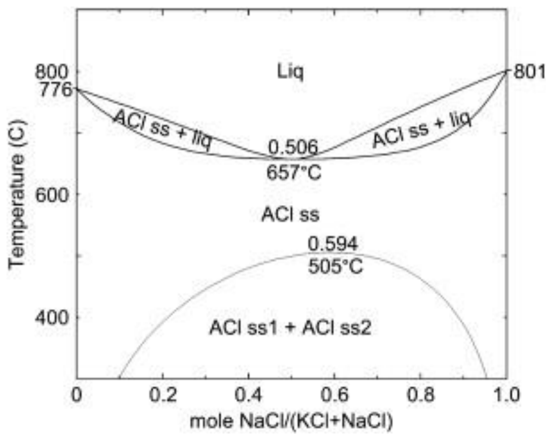

Fig.1. Phase diagram of NaCl-KCl mixed chlorine salt [1]

The extreme condition 800℃ has the highest internal energy and is the optimal condition to damage the structural materials. After corrosion immersion test for 48 hours at 800°C higher than the chlorine-based MSR operating temperature, residual salts adhering to the surface of the structural material were removed by rinsing with distilled water.

2.2 Analysis before/after corrosion immersion test

Damage, discoloration, and roughness of the structural material surface before and after the After-corrosion immersion test were confirmed by naked eye. Mapping grain boundary behavior and pinholes with SEM (Scanning Electron Microscopy) and surface element distribution changes with EDX (Energy-Dispersive X-ray spectroscopy). The structural stability of the parent material was verified by XRD (X-Ray Diffraction) peak matching. AFM (Atomic Force Microscopy) classified the damaged layer and the metal oxide layer by surface integrity and average thickness.

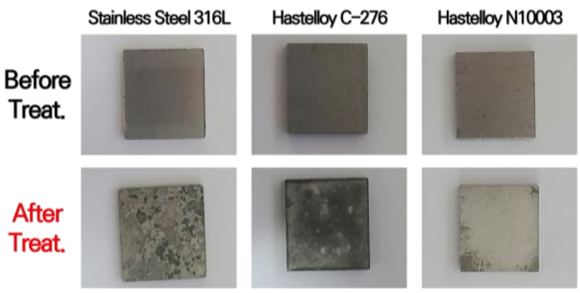

Fig.2. Naked eye vision image of before/after corrosion immersion test

2.4 Results and discussion

Under the extreme operating conditions of MSR, the starting point of intergranular corrosion of the alloy is the pinhole of the grain boundary. The alloy maintains a dense surface by forming an oxidation protective layer according to each characteristic. The grain boundary change for the three alloys of the structural material candidate group was confirmed by AFM. In Stainless Steel 316L, a metal oxide layer was formed by salt while the protective layer was removed, and the Cr-oxide layer on the surface was not uniform. It was confirmed that Iron-based ions were eluted by the molten salt. As a result of confirming the average surface thickness, it was confirmed that the oxide layer increased about 8 times compared to the protective layer. That is, the change of grain boundaries after the reaction, removal of the protective layer, and the formation of a metal oxide layer showed that Stainless Steel collapsed. Hastelloy®-based metal is mixed with Ni-Cr-Mo to have a higher density of surface elements compared to Stainless Steel 316L. In particular, C-276 exhibits high elongation and reduced thermal expansion due to the addition of trace elements. In addition, there was almost no change in surface mean thickness before and after reaction in chlorine-based salts under the influence of Ni element, which is the main component. N10003 also contains trace elements, but they are for mechanical stability (tensile strength and yield strength), not chemical stability (formation of surface protective layer). Therefore, many pinholes were formed, and it can be inferred that the chemical stability was not high because residual salts were detected here. In the AFM analysis results, it was found that as ions escaped, the surface anti-oxidation layer rapidly decreased, and the average surface thickness of the center also decreased.

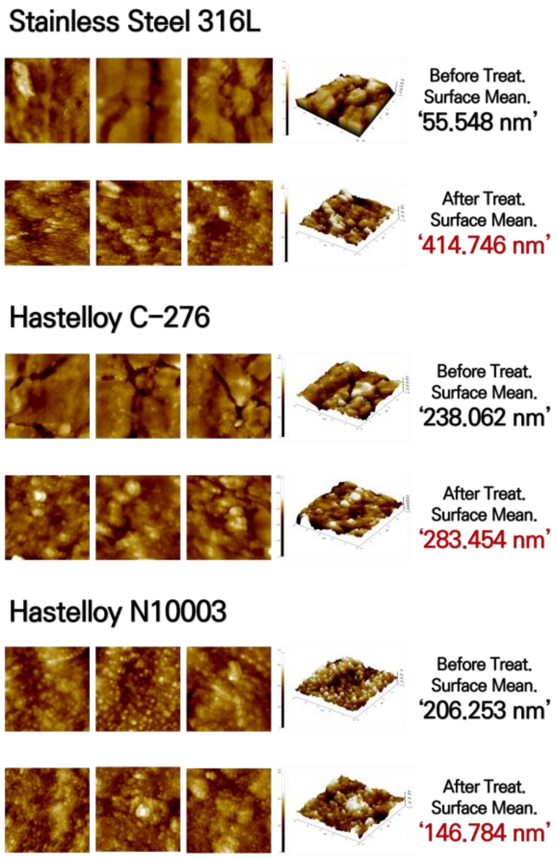

Fig.3. AFM of structural materials before/after 0.506M NaCl – 0.494M KCl molten salt treatment for 48 hours at 800°C

3. Conclusions

We investigated and analyzed corrosion immersion tests for three candidate groups to find the most suitable structural material for MSR. The suitable condition of the structural material is the anti-oxidation layer on the surface and the fewer pinholes are formed at the grain boundary, the more it has corrosion resistance from chlorine-based salts. Therefore, as a structural material for chlorine-based MSR, nickel-based alloys such as Hastelloy® not only improve mechanical strength but also increase the stability of the surface structure by addition trace elements. Ni-Cr-Mo in the form of a surface barrier has improved structural stability at high temperatures and corrosion resistance at surface grain boundaries by adding V (Vanadium), W (Tungsten) as microelements of C-276. The effect of preventing chlorine corrosion was confirmed due to the use of an alloy containing a minimum of Fe ions. In conclusion, Hastelloy® C-276 is the most suitable structural material for the long-term operation of MSR among candidates. However, it is difficult to directly apply to MSR due to minor surface damage to the surface. Therefore, in future research, the commercialization of MSR can be expected after improving the corrosion resistance of chlorine-based salts as a surface coating of structural materials.

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