

A study on corrosion behavior of structural material in molten salt with lithium

Mingue Lee^a, Jisu Na^a, Jeong Hye Jo^a, and Young Soo Yoon^{a*}

^aDepartment of Materials Science and Engineering, Gachon University, Gyeonggi-do, 13120

*Corresponding author: benedicto@gachon.ac.kr

1. Introduction

Nuclear power plant suitable for the Net-Zero policy is required a lot of research due to surging fuel prices and depletion. Among them, MSR, the next-generation nuclear power plant, uses liquid molten salt as nuclear fuel and high-temperature coolant. MSR integrates nuclear fuel and coolant. So, the major accident in which radioactive material is leaked is fundamentally excluded. And the operating environment is normal pressure and high temperature. [1-2] Therefore, MSR is superior in stability and thermal efficiency compared to light-water reactors. As the molten salt for cooling, a fluorine-based salt is mainly used. On the other hand, chlorine-based salts target white hydrogen production and passive natural circulation at an operating temperature of about 100°C higher than fluorine-based salts. However, molten chloride salt is corrosive at high temperatures, so corrosion resistance of structural materials is required for long-term operation. One of the most important aspects to understand for structural corrosion resistance of MSR is the temperature of the molten salt. When the temperature of the molten salt during operation is significantly higher than the eutectic point, corrosion is accelerated, causing problems in long-term operation. Therefore, the structural material corrosion proof is performed with the residual energy applied to the change in the melting point of the salt.

2. Methods and Results

2.1 Preparation of chlorine salt immersion test

Stainless Steel 316L, Hastelloy of Hynes® C-276, and N10003 metal alloy plates were prepared by cutting 1 cm² for chlorine-based mixed salt corrosion testing. After the rinsing process, three structural material candidates in an alumina crucible were tested for corrosion with two salts. Corrosion tested with two salts. The first salt is 0.506NaCl-0.494KCl mixed chlorine salt with a eutectic point of melting temperature at 657°C and this salt is called C1NaK. The second salt is 0.100LiCl-0.455NaCl-0.445KCl, and this salt is called C1LiNaK. The C1NaK, and C1LiNaK salts were placed in the alumina crucible to confirm that the melting points of the two salts tested for corrosion were similar to the phase diagram. In order to find the melting point of C1LiNaK, the temperature was heat-treated from 540°C to 600°C at 20°C intervals.

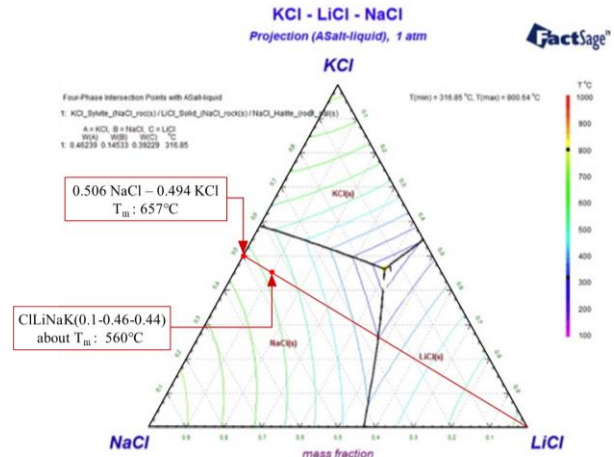


Fig. 1. Phase diagram of NaCl-KCl-LiCl mixed salt. [3]

2.2 Resin mounting and polishing

The heat treatment conditions of the two corrosion tests were the same at 800°C, and after the corrosion test for 48 hours, residual salts attached to the surface of the structural material were removed by rinsing with distilled water. For polishing, grinding was performed in the order of 180, 320, 600, and 800 grit Silicon carbide (SiC) as sandpaper. After that, polish to 9,3, and 1 micrometer size with diamond suspension.

2.3 Analysis of chlorine-based salt corrosion

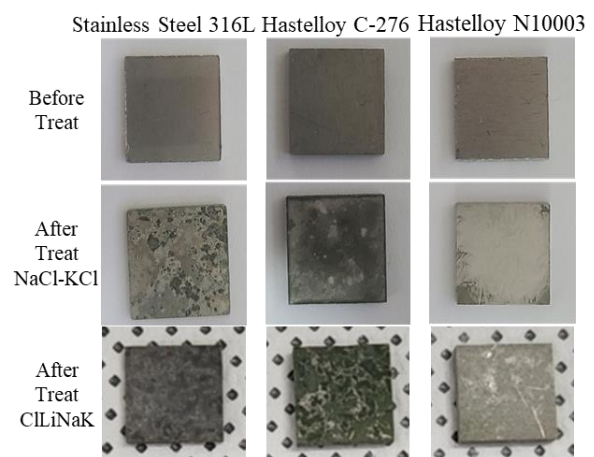


Fig. 2. Visual images of the three-candidate alloy before-after corrosion immersion test

The C1LiNaK salt corrosion test was visually observed before and after. Immersion corrosion with LiCl salt in NaCl-KCl maximizes surface damage.

Surface damage causes the metal to elute at the grain boundary due to the energy difference given excessively as the melting point is lower. The eluted metal precipitates on the metal surface and is ionized in the salt. Discriminating the difference between before and after the corrosion test and the degree of corrosion due to the difference in the composition of the molten salt is workable. However, discriminating the degree of corrosion of different substrates in the same molten salt composition is difficult

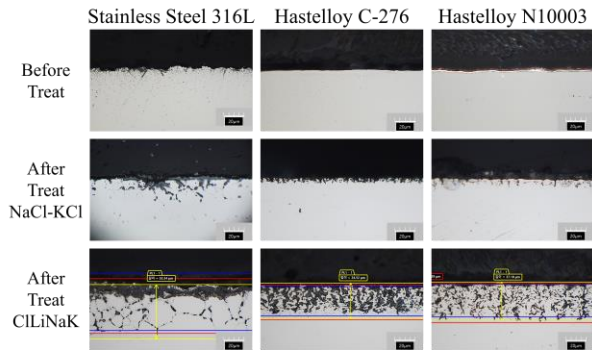


Fig. 3. OM images of the three Candidate alloys before-after corrosion immersion test

The OM image shows the difference in corrosion depth before and after immersion corrosion testing. Although the same 48h and 800°C corrosion tests were performed, the difference in salt corrosion depth of CILiNaK, which has a melting point of about 100°C lowers, is about 4 times or more. as well as SEM image cross-section analysis. In the image, the corrosion pattern appears completely different. Due to the different melting points and different salt compositions, the corrosion forms are different. [4] The SUS substrate appears to be corroded along the grain boundary. And pitting corrosion appears in several places. Hastelloy's substrates are shaped in such a way that some of the constituent metal components are corroded. Certain components are selectively corroded. The rest of the metal remains.

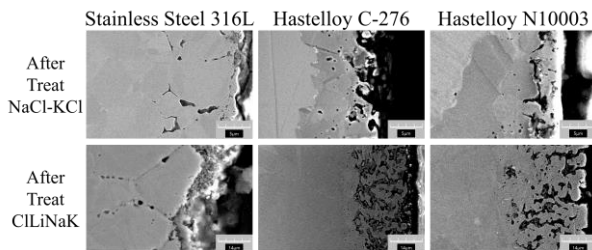


Fig. 4. SEM of Cross-section of the three Candidate alloys before-after corrosion immersion test

2.4 Corrosion behavior results and discussion

During MSR operation, corrosion test was conducted for long-term operation, and according to Gibbs free energy, Ni has a lower ionization tendency than Cr and

Fe. However, the lower the melting point of the molten salt, the higher the degree of corrosion must be approached through the same heat capacity-operating temperature as Prandtl number other than the Gibbs free energy. CILiNaK has a lower eutectic point than CINaK and contains LiCl, so phase change energy is converted into thermal energy, providing a fast diffusion path for ions. The iron-based alloy showed a lower corrosion tendency in the molten salt containing LiCl salt, but the Ni-based alloy was depleted ion elution occurred continuously. The molten salt does not match the Gibbs free energy in the Ni-based alloy because it receives energy of about $\Delta 240^\circ\text{C}$ (800-560°C), thus providing a favorable corrosive environment.

Table 1. Gibbs free energy of Na, Li, K with chlorine

	Na+1/2Cl ₂ →NaCl	Li+1/2Cl ₂ →LiCl	K+1/2Cl ₂ →KCl
ΔH	-411.0 (KJ/mol)	-408.3 (KJ/mol)	-435.9 (KJ/mol)
ΔS	-0.091 (KJ/mol)	-0.081 (KJ/mol)	-0.093 (KJ/mol)
T ₁	298.15 (K)		
ΔG_1	-384.0 (KJ/mol)	-384.0 (KJ/mol)	-408.0 (KJ/mol)
T ₂	1073 (K)		
ΔG_2	-313.8 (KJ/mol)	-321.0 (KJ/mol)	-335.6 (KJ/mol)

Additionally, Gibbs free energy of chlorine-based salt as shown in the table 1., Lithium, sodium, and calcium are not significantly different. In order to understand the relationship between Prandtl numbers, further analysis is needed on the relationship between temperature and viscosity in liquids.

3. Conclusions

The energy provided to the molten salt reduced to a minimum the corrosion acceleration of the structural material. Altogether, MSR recommends combining molten salt with an operating temperature close to the operating temperature. However, the viscosity or heat transfer efficiency may decrease and should be considered through simulation. In addition, since the viscosity effect of the liquid cannot be excluded due to the drop in the melting point due to the addition of LiCl, further experiments should be conducted. In conclusion, this study suggests that the operating temperature and salt composition of MSR molten salt are important for corrosion optimization of structural materials.

REFERENCES

- [1] Kim, Jong Woo, et al. "Study of structural stability at high temperature of pseudo-single tube with double layer as an alternative method for accident-tolerant fuel cladding." *Journal of Nuclear Materials* (2022): 153800.
- [2] Cervi, E., et al. "Development of a multiphysics model for the study of fuel compressibility effects in the Molten Salt Fast Reactor." *Chemical Engineering Science* 193 (2019): 379-393.
- [3] Wu, Jie, et al. "The influence of NaCl concentration on the (LiCl-KCl) eutectic system and temperature

dependence of the ternary system." *Journal of Molecular Liquids* 253 (2018): 96-112.

[4] Redkin, A., et al. "Heat of fusion of halide salts and their eutectics." *Journal of Thermal Analysis and Calorimetry* 131.2 (2018): 2021-2026.3

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. NRF-2021M2D2A2076384)