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

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1. Abstract

- The MSR (Molten Salt Reactor) is a 4^{th} generation nuclear reactor that is currently being noticed due to its low vapor pressure, white hydrogen generation, high operation stability, and thermal efficiency.
- In the case of chlorine-based salts, compared to fluorine-based salts, which are mainly studied, *1) high-energy operation is possible, 2) white hydrogen production is possible at the same time, and 3) inexpensive*, so it is attracting nuclear field researchers' attention.
- Mechanical strength, high-temperature heat resistance, and excellent corrosion resistance at chlorine-based salts condition are essential properties of chlorine-based MSR structural materials.
- In this study, to find a structural material suitable for the long-term operation of MSR, three candidate materials were selected, and corrosion immersion tests was performed on NaCl-KCl molten salt.

2. Theory & Experimental

◆ Mechanical strength of substrates and chemical salt gradient

Table 1. Mechanical strength of selected three structural materials[1)]

	Stainless Steel 316L	Hastelloy C-276	Hastelloy N10003
Melting range	1,400℃	1,370℃	1,400℃
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

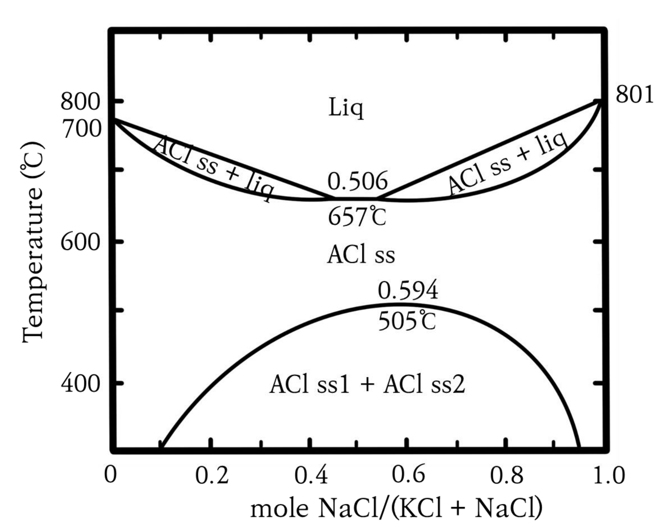

Fig. 1. Binary phase diagram of KCl-NaCl.[2)]

◆ Thermodynamic behavior of corrosion resistance

Table 2. Gibbs free energy of formation per molecule Cl_2 for various chlorides at 800°C

Reactions	Gibbs free energy (△G)
$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$	-627.5 kJ/mol
$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$	-671.1 kJ/mol
$Cr(s) + Cl_2(g) \rightarrow CrCl_2(s)$	-254.5 kJ/mol
$2/3Cr(s) + Cl_2(g) \rightarrow 2/3CrCl_3(s)$	-202.8 kJ/mol
$Fe(s) + Cl_2(g) \rightarrow FeCl_2(s)$	-199.8 kJ/mol
$2/3Fe(s) + Cl_2(g) \rightarrow 2/3FeCl_3(s)$	-109.3 kJ/mol
$Ni(s) + Cl_2(g) \rightarrow NiCl_2(s)$	-138.7 kJ/mol
$W(s) + Cl_2(g) \rightarrow WCl_2(s)$	-122.9 kJ/mol

- Arrhenius equation

$$K(T) = A \cdot exp(-\frac{E_a}{RT})$$

K(T) : Reaction rate (1/sec) T : Absolute temperature (K)
A : Arrhenius velocity constant R : Gas constant (8.314J/mol·K)
E_a : Activation energy (J/mol)

- Metal-Cl production mechanism

$M + 2Cl^- \rightarrow MCl_2 + 2e$
$MCl_2 + M^{2+} \rightarrow 2Cl^-$

◆ Corrosion immersion test in 0.506 NaCl – 0.494 KCl at 800°C

Table 3. Compositions of three structural materials[3)]

	Stainless Steel 316L	Hastelloy C-276	Hastelloy N10003
Fe	Bal.	5	4*
Ni	10.0-14.0	Bal.	Bal.
Cr	16.0-18.0	16	7
Mo	2.0-3.0	16	16
Mn	2.0	1*	0.8*
Si	0.75	0.08*	1*
C	0.03	0.01*	0.06
Cu	–	0.5*	0.35*
Co	–	2.5*	0.02*
W	–	4	0.5*
V	–	0.35*	0.5*
N	0.1	–	–
P	0.045	–	–
S	0.03	–	–

* refers to the maximum amount of component to be contained.

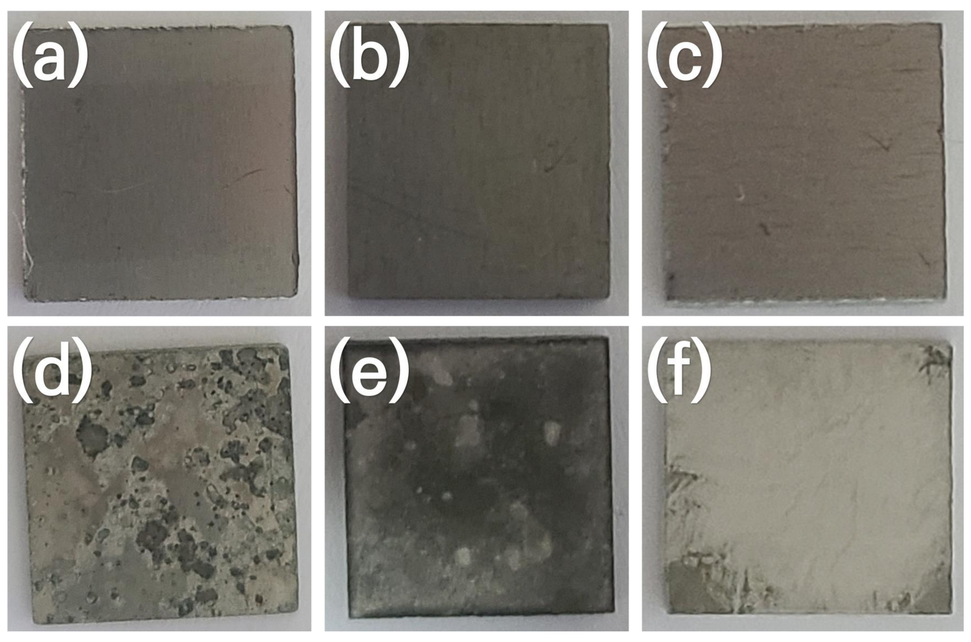

Fig. 2. Vision image of before and after corrosion immersion test for 48 h at 800°C. ; Before/After : Stainless Steel 316L (a)/(d), Hastelloy C-276 (b)/(e), Hastelloy N10003 (c)/(f)

Acknowledgement

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Reference

1) "AZO Materials.", Stainless Steel-Grade 316L-Properties,https://www.azom.com
2) Broström, Markus, et al. "Condensation in the KCl-NaCl system." Fuel processing technology 105 (2013): 142-148.
3) "HAYNES INTERNATIONAL.", https://www.haynesintl.com/alloys/alloy-portfolio_/Corrosion-resistant-Alloys

3. Results & Discussion

◆ Surface morphology analysis of before and after corrosion test

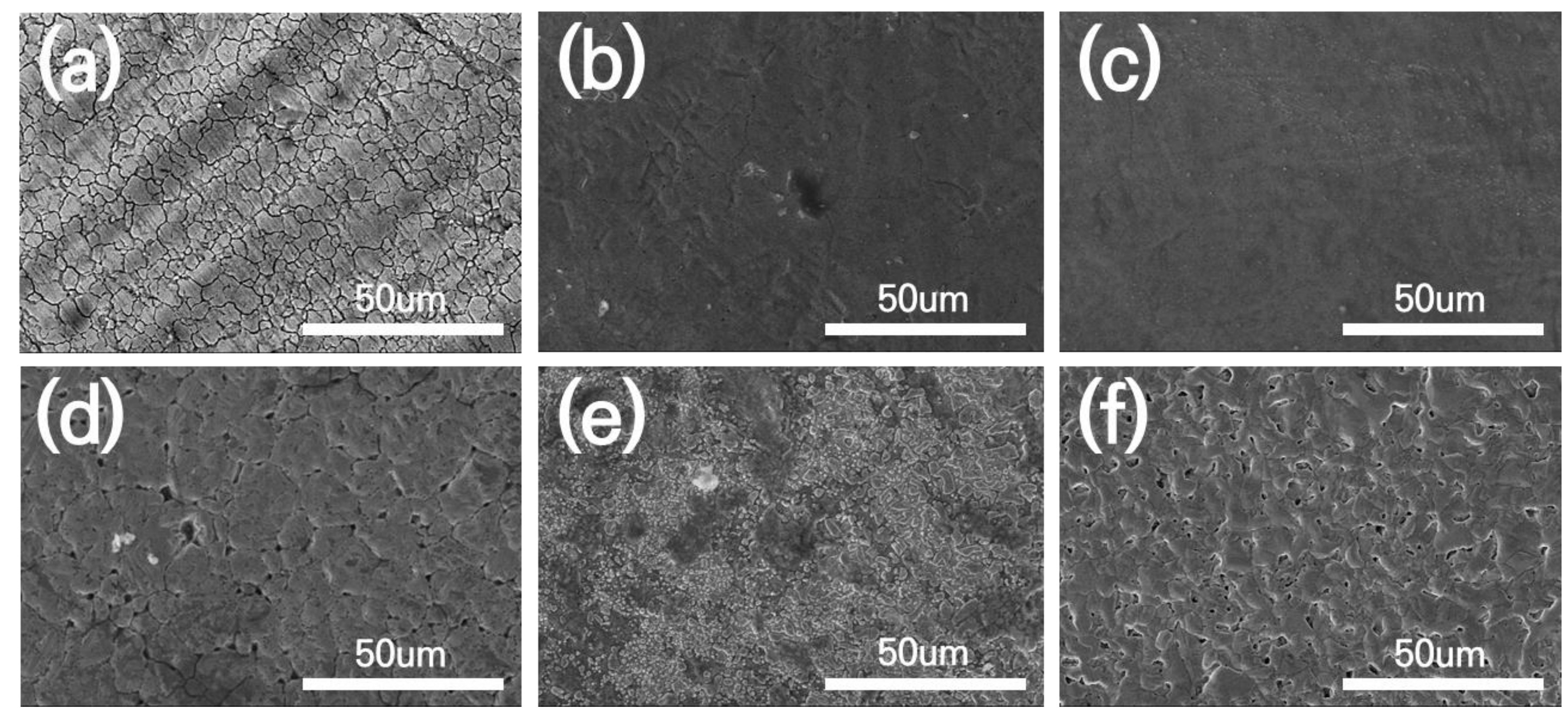

Fig. 3. SEM image of before and after corrosion immersion test for 48 h in molten salt at 800°C.
; Before/After : Stainless Steel 316L (a)/(d), Hastelloy C-276 (b)/(e), and Hastelloy N10003 (c)/(f)

Table 4. Structural materials surface mean thickness change of before/after corrosion immersion test for 48 h at 800°C

	Stainless Steel 316L	Hastelloy C-276	Hastelloy N10003
Before	55.548 nm	238.062 nm	206.253 nm
After	414.746 nm	283.454 nm	146.784 nm

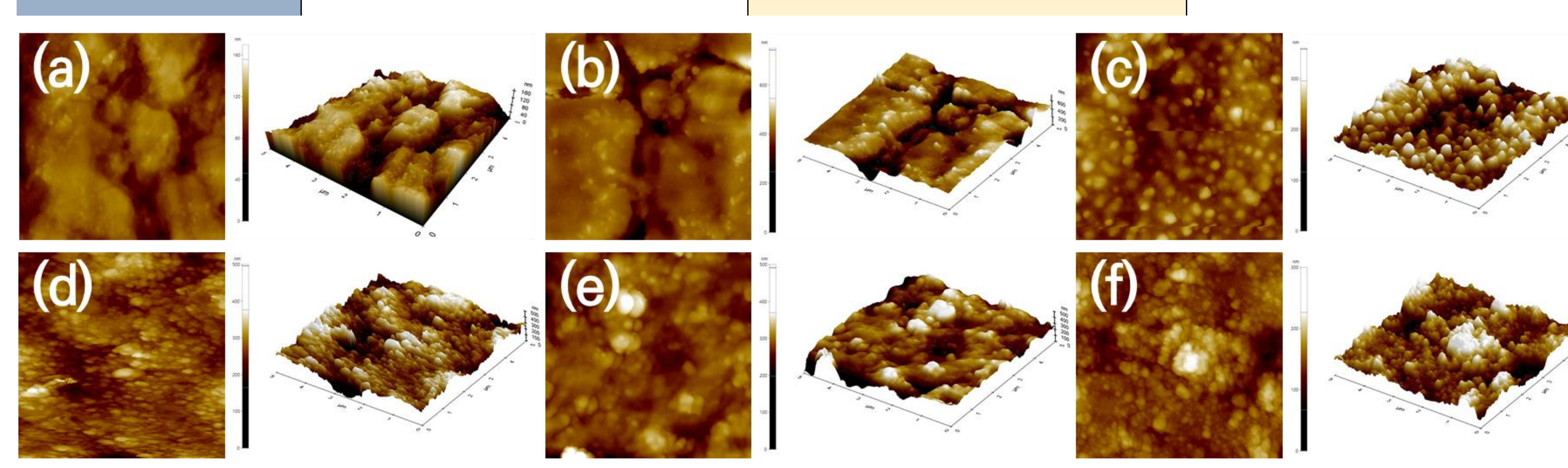

Fig. 4. AFM image of before and after corrosion immersion test for 48 h in molten salt at 800°C.
; Before/After : Stainless Steel 316L (a)/(d), Hastelloy C-276 (b)/(e), Hastelloy N10003 (c)/(f)

◆ Compositions change of before and after corrosion test

Table 5. Corrosion rate by amount of ion eluted corrosion immersion test

	Stainless Steel 316L	Hastelloy C-276	Hastelloy N10003
Fe	2.29×10^{-4}	1.00×10^{-4}	4.79×10^{-5}
Ni	1.19×10^{-5}	3.96×10^{-5}	1.75×10^{-5}
Cr	4.38×10^{-5}	4.79×10^{-5}	2.92×10^{-5}
Mo	2.00×10^{-6}	7.08×10^{-6}	1.50×10^{-5}
24h	2.33×10^{-4}	2.08×10^{-5}	1.67×10^{-4}
48h	4.67×10^{-4}	8.33×10^{-5}	3.34×10^{-4}

* Corrosion rate formula of calculation = $g/m^2 \cdot h$

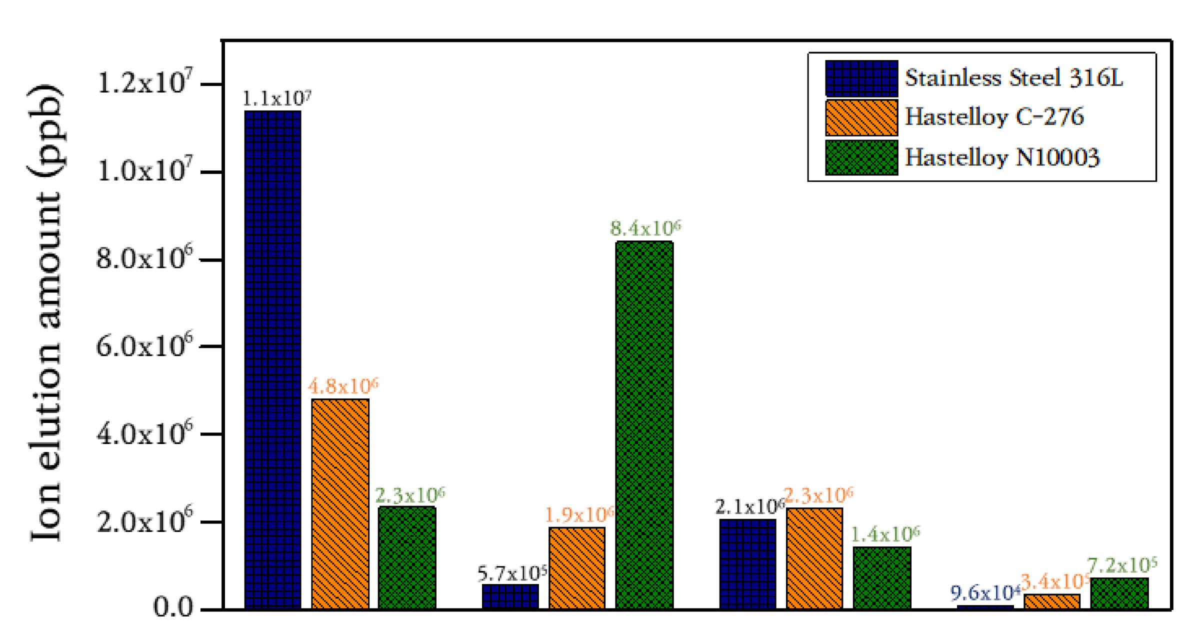

Fig. 5. Amount of ion eluted from the substrates after the corrosion immersion test for 48 h in molten salt at 800°C.

4. Conclusion

- According to the results, Stainless Steel 316L is not suitable as a structural alloy for MSR because of the elution of Fe-ions.
- In the case of each Ni-based material with different Cr contents, the role of trace elements was identified to be important because the elution of Ni-ions became a problem, contrary to the prediction of the Gibbs free energy calculation.
- Hastelloy C-276 containing a trace elements Co (Cobalt), W (Tungsten), etc. in the Ni-Mo-Cr layer was the best effective for Cl-based salt anti-corrosion, surface and structural stability.
- However, Hastelloy C-276 is also considered to be limited in its direct application to long-term MSR due to the size and shape change of grain length and boundary microstructure.
- Therefore, it needs necessary to supplement these problems with the surface coating of Hastelloy C-276 in further research.

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